

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09K 5/04		A1	(11) International Publication Number: WO 97/11138 (43) International Publication Date: 27 March 1997 (27.03.97)
(21) International Application Number: PCT/US96/14882 (22) International Filing Date: 17 September 1996 (17.09.96)		(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, TT, UA, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(30) Priority Data: 60/004,038 21 September 1995 (21.09.95) US 60/006,145 2 November 1995 (02.11.95) US 08/611,258 5 March 1996 (05.03.96) US		(71)(72) Applicant and Inventor: GOBLE, George, H. [US/US]; 286 West Navajo, West Lafayette, IN 47906 (US). (74) Agents: BROWNING, Clifford, W. et al.; Woodard, Emhardt, Naughton, Moriarty & McNett, Bank One Center/Tower, Suite 3700, 111 Monument Circle, Indianapolis, IN 46204 (US).	
Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>			
(54) Title: DROP-IN SUBSTITUTES FOR DICHLORODIFLUOROMETHANE REFRIGERANT			
(57) Abstract <p>A group of known refrigerants, (R-227ea, R-124, R-134a, R-143a, R-125, R-E125, R-E143a, R-E227ca2, R-245cb, R-600a, R-142b, R-22, R-290, R-E170, R-1270, R-1216, R-218, R-C318, R-C270) that may be combined in novel ways to produce several excellent "drop-in" substitutes for refrigerants R-12 or R-500. The performance of the preferred "drop-in" substitutes for R-12 or R-500 of the present invention often exceeds that of the refrigerant being replaced, while maintaining acceptable oil circulation with existing mineral oils used in R-12 or R-500 refrigeration and air conditioning systems.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**DROP-IN SUBSTITUTES FOR
DICHLORODIFLUOROMETHANE
REFRIGERANT**

5 The present invention relates to refrigerants generally, and more specifically to a mixture of refrigerants that may be substituted for the environmentally damaging refrigerant dichlorodifluoromethane (R-12).

BACKGROUND OF THE INVENTION

10 In order to provide a more compact format for identifying mixtures of refrigerants in the following discussions, mixtures of refrigerants will be listed in the form of:

R-ABC/DEF/GHI N0/N1/N2

15 which represents a mixture of refrigerants (fluids) R-ABC, R-DEF, and R-GHI where N0, N1, and N2 are the weight percentages of each component refrigerant fluid, and $N0+N1+N2 = 100$; or in the form of:

20 R-ABC/DEF/GHI N0-N0'/N1-N1'/N2-N2'

which is similar, but specifies ranges of the weight percentages each of the component refrigerant fluids, with the total of the weight percentages being 100 percent.

25 Zeotropic (nonazeotropic) mixtures of refrigerants will change composition if they are allowed to leak as vapor phase from a container containing all components of the refrigerant mixture in both vapor and liquid phases. Single component and azeotropic mixtures of refrigerants do not change composition appreciably from vapor leakage. Single component and azeotropic mixtures of refrigerants have only one boiling point temperature for a given pressure, provided the refrigerant exists as both liquid and vapor states in the container. Zeotropic mixtures of refrigerants will boil over a range of temperatures at a given pressure. As the temperature is raised, the

point at which the first bubbles appear (constant pressure) in the liquid is known as the "bubble point," which is roughly analogous to the boiling point of a single component or an azeotropic mixture. Starting in a vapor phase and lowering the temperature (at a constant pressure) to the point where the first 5 droplet of liquid forms defines what is known as the "dew point" of the mixture of refrigerants. The difference between the bubble point temperature and the dew point temperature is known as the temperature "glide". A pressure gauge connected to a cylinder containing a zeotropic mixture of refrigerants will read the bubble point pressure for the corresponding temperature of the 10 refrigerant mixture.

Under the Montreal Protocol, as amended, United States laws (1990 Clean Air Act), and U.S. Environmental Protection Agency rules, the production and importing of R-12 ended on December 31, 1995. Additionally, only 15% of the 1989 baseline amounts of chlorinated fluorocarbons (CFCs) 15 was allowed to be produced or imported into the U.S. during the year 1995 adjusted on an ozone depletion factor basis. R-12 is the major share of that production.

With the effective date of the ban on U.S. R-12 production and 20 importing having passed (December 31, 1995), one industry option has been to retrofit R-12 refrigeration or air conditioning systems, both stationary and automotive, to R-134a (tetrafluoroethane). The mineral oils used in R-12 systems are completely immiscible in R-134a, however, as the industry has therefore developed new oils, which are either polyalkylene glycol (PAG) 25 based (for automotive) or polyol ester (POE) based (stationary refrigeration and some automotive retrofit).

While PAG oils are good lubricants, and are miscible in R-134a at typical evaporator temperatures, they have two main problems. First, most PAG oils cannot tolerate even minute traces of residual chlorides that remain

in the R-12 refrigeration or air conditioning systems that have been purged of R-12. These chlorides are dissolved in the small amount of mineral oils which cannot be flushed out or are in coatings on the inside of aluminum piping (aluminum chloride from previous R-12) or are dissolved in rubber hoses. The 5 presence of chlorides greatly accelerates the breakdown of most PAG oils.

It has been reported in the literature that test systems that were flushed with R-11 (trichlorofluoromethane) and then retrofitted to PAG oil and R-134a, sustained catastrophic compressor failures within one week due to oil breakdown. R-11 has a greater affect on PAG oil breakdown than does R-

10 12. It was common practice in the automotive air conditioning service industry, into the early 1990s, to flush R-12 systems with R-11 to remove contaminates. The traces of R-11 remaining do not interfere with R-12 operation, but could cause premature failures if R-12 systems are ever retrofitted to R-134a and PAG oils.

15 The second main problem with PAG oils is that PAG oils are in the order of 100 times more hydroscopic (absorb moisture) than are R-12 mineral oils. During assembly, service, or after an accident, automotive R-134a systems may be exposed to atmospheric moisture which will be absorbed into the PAG oil. Extreme care is therefore required during servicing of PAG oil 20 systems to prevent exposure to atmospheric moisture, especially in humid climates.

The stationary refrigeration industry has overwhelmingly chosen POE-based oils for R-134a systems, for both new systems and those retrofitted from R-12. POE oils can tolerate residual chlorides much better than PAG 25 oils, however POE oils have problems also. POE oils are on the order of 10 times more hydroscopic than are R-12 mineral oils. POE oils, in general, do not have as good lubricities as do the PAG and mineral oils. Steel is a known catalyst that facilitates the breakdown of most POE oils at the higher

-4-

temperatures encountered in refrigeration systems. The industry has had to develop passivators and additive packages for POE oils to try to counter this problem. Moisture and other contaminates may cause the POE oils to break down into their constituent fatty acids and alcohols.

5 Many industry R-134a retrofit procedures for R-12 stationary refrigeration and air conditioning systems call for 3 to 5 changes of the compressor oil (to a POE) in order to reduce the residual mineral oil to below about 1 percent to about 5 percent by volume. Most small to medium sized (up to 10 tons in capacity) hermetic compressors in R-12 equipment do not have oil drains. Therefore, the compressor must often be removed and the oil dumped out up to 5 times for a retrofit to R-134a. This entails unbrazing the low and high side refrigeration pipes from the compressor and rebrazing them up to 5 times. The brazing temperature is about 1100 degrees Fahrenheit. Service technicians often do not go to the trouble to bleed a relatively inert 10 gas such as dry nitrogen or CO₂ through the piping during brazing operations. Brazing temperatures cause the copper piping to oxidize on the inside forming "scale" which flakes off and adds to the contamination of the system. The oil coating the inside of the piping breaks down and carbonizes, adding more contaminates. Even worse, if refrigerant vapors are present in 15 the pipes during brazing, they decompose into hydrochloric and hydrofluoric acids, which greatly add to system contamination and premature failure. Finally, the physical operation of removing the compressor 5 times, and inverting it to remove oil, can allow metal flakes and other sludge which have accumulated in the bottom of the compressor oil sump to break loose and end 20 up on the top of the inside of the compressor shell. Upon reinstalling the compressor this sludge and metal flakes may drop onto the top of the compressor and get into motor windings (causing shorts and motor burnouts) or get into the intake valves and cause mechanical problems (seized 25 compressor).

-5-

There have been several reports that both POE and PAG oils causing skin rashes or burns to service technicians. This has necessitated additional safety procedures, such as wearing gloves, when handling these oils. Unless a hermetic compressor motor burnout has occurred, R-12 mineral oils have not caused skin rashes and burns to service technicians. A hermetic compressor motor burnout causes some of the refrigerant to decompose into hydrofluoric and hydrochloric (if the refrigerant contains chlorine atoms) acids, and may cause skin burns no matter what oil is used.

Some compressors built for R-12 and retrofitted to R-134a with POE oils have been reported by compressor manufacturers to fail from lubrication problems caused by the lack of the "foaming" of the POE oils in the compressor crankcase. Some compressor designs relied on the fact that mineral oils and R-12 generated foaming in the compressor crankcase in order for the oil to reach and lubricate certain parts of the compressor. New compressors designed for R-134a and POE oils use other means to make sure all the parts are properly lubricated.

Compressors manufactured for R-12 and mineral oil use often were constructed with a paraffin based wax coating on the motor windings as an aid to building the motor without breaking the wire during the motor winding phase of the construction. When retrofitted to R-134a and POE oils, the paraffin would sometimes come off the windings, and not dissolve in the R-134a refrigerant and POE oils, and circulate through the system as solids and plug up the refrigerant metering device, usually a capillary tube, causing the system to fail. R-12 (or a substitute with adequate mineral oil miscibility) and mineral oil, just dissolve the pieces of paraffin wax which come off the motor windings and therefore do not clog the refrigerant metering device.

Finally, the low critical temperature of R-134a (213.9 degrees Fahrenheit) verses the critical temperature of R-12 (233.2 degrees

-6-

Fahrenheit) can cause abnormally high head pressures in hot ambient conditions in systems designed for R-12. For automotive applications, stopped traffic or hot climates can cause a reduction in R-134a performance.

5 Systems designed for R-134a often increase the size of the condenser about 50 percent over the size similarly designed R-12 system condenser. Stationary systems, such as vending machines, now retrofitted to R-134a may see high head pressure and low performance problems when the condenser becomes slightly fouled by dirt and dust. R-12 systems can run much longer between cleanings to remove dust and dirt from the condenser

10 than similar systems converted to R-134a.

R-406A is a known ternary mixture of refrigerants, consisting of isobutane (R-600a), chlorodifluoroethane (R-142b), and chlorodifluoromethane (R-22) that provides a "drop-in" substitute for dichlorodifluoromethane (R-12) refrigerant. R-406 is described in U.S.

15 Patent Nos. 5,151,207 and 5,214,929, the disclosures of which are incorporated herein by reference.

20 In addition to being a suitable "drop-in" substitute for R-12, R-406A has been successfully used as a "drop-in" substitute for refrigerant R-500 (azeotropic mixture of R-12 and R-152a with weight percentages of 73.8 and 26.2, respectively) in many instances. R-152a is 1,1-difluoroethane.

25 Refrigeration systems with refrigerant metering devices consisting of a capillary tube or a fixed orifice have had excellent results with R-406A as a "drop-in" substitute. Some R-500 systems with "thermostatic expansion valves" (TEVs), have needed the "power head" of the expansion valve changed to an R-12 head, while others have performed satisfactory.

Several other attempts have been made to create the ideal "drop-in" substitute for R-12. Some do not return mineral oil to the compressor properly at temperatures of desired operation (i.e., Forane® FX-56 (R-

124/142b/22 25/15/60) also known as R-409A, U.S. Patent No. 5,188,749; and FRIGC™ FR-12™ (R-600/124/134a 2/39/59), U.S. Patent No. 5,425,890). Changing the compressor oil from mineral oil to alkylbenzene oil will often correct the oil return problems, but now an oil change is necessary and the 5 refrigerant is no longer a "drop-in" substitute for R-12.

Some attempts have provided temperature-pressure curves which are not always suitable for operation of R-12 equipment. The Forane® FX-56 refrigerant temperature-pressure curve is too high, which results in excessive head pressures, refrigerant breakdown and compressor failures in many 10 instances. See Figure 1 for the Forane® FX-56 temperature-pressure chart. FRIGC™ FR-12™, on the other hand, has a temperature-pressure curve which is too low, which results in low system capacities, and causes problems if system low pressure cut out controls are not replaced or adjusted. See Figure 1 for the FRIGC™ FR-12™ temperature-pressure chart. FRIGC™ FR- 15 12™ used in an automotive air conditioning system should produce suction side pressures of about 18 to about 23 gauge pressure (PSIG), whereas R-12 would produce about 28 to about 32 PSIG. This causes the low pressure controls to prematurely open, falsely sensing low-on-charge or too cold conditions. Once opened, the compressor clutch disengages, stopping the 20 compressor, and the system equalizes in pressure, and restarts. This results in poor capacities, and excessive clutch wear from cycling every few seconds. Automotive variable displacement compressors, such as the GM V-5, try to maintain a constant suction pressure, usually about 28 to about 30 PSIG for capacity control. The lower than R-12 temperature-pressure curve of 25 FRIGC™ FR-12™ fools these compressors into operating at a much lower displacement than for R-12 under given load conditions, thus greatly reducing capacities (in the order of 50 percent reduction or more). If a large amount of FRIGC™ FR-12™ (3 pounds or more), is allowed to vapor leak under ambient temperatures of about 10 degrees to about 25 degrees Fahrenheit, the

-8-

remaining mixture may possibly first go weakly flammable then highly flammable near the very end of the leak out (90 weight percent or more of the mass has leaked). The boiling point of their highest boiling point component, R-600 (n-butane), is 31.03 degrees Fahrenheit, while their next lower boiling point component is R-124, with a boiling point of 8.26 degrees Fahrenheit.

These foregoing and additional known refrigerant mixtures are summarized below. Some are disclosed in research papers and others in U.S. Patents, while still others are commercial products on the market.

R-124/22 60/40

10 Has poor mineral oil miscibility. See U.S. Patent no. 4,303,536.

R-124/125 65/35

Almost nonexistent mineral oil miscibility, and the glide is too high.

R-124/142b/22 25/15/60

This is Elf Atochem Forane® FX-56, or R-409A. See U.S. Patent No.

15 5,188,749. Forane® FX-56 has poor mineral oil miscibility, and the temperature-pressure curve is too high. It is sometimes claimed to be an R-12 "drop-in", other times claimed to be near "drop-in" requiring changing oil to alkylbenzene type to assure miscibility. Six hours of operation in the oil miscibility test stand described in Appendix A, caused moderate oil logging in
20 the evaporator and suction line at an evaporator temperature of about 10 degrees Fahrenheit using Suniso 3GS (150 viscosity) mineral oil, standard for systems of this type. Severe oil logging occurred around -20 degrees Fahrenheit, with two phase (oil and liquid refrigerant) and "milky" solutions observed in the evaporator. Pure R-22 performed much the same way. The
25 "milky" solution is caused by an immiscible "dispersion" of oil and liquid refrigerant. After severe oil logging from Forane® FX-56 at about -20 degrees Fahrenheit, the Forane® FX-56 was removed, and the oil miscibility test stand was charged with the refrigerant mixture later described in Example 1.

-9-

Two hours of operation with Example 1 returned almost all the oil to the compressor, operating at about -30 degrees Fahrenheit.

R-22/124/142b 65/25/10

This is Elf Atochem Forane® FX-57, or R-409B. This mixture will have even

5 less miscibility in mineral oil than Forane® FX-56. Forane® FX-57 will also have an even higher temperature-pressure curve than Forane® FX-56 due to more R-22 component and less R-142b component.

R-124/152a/22 24/13/53

This is DuPont SUVA® MP-39, or R-401A. See U.S. Patent No. 4,810,403.

10 R-401A has poor miscibility in mineral oils. DuPont recommends at least 80 volume percent of the compressor oil be changed to alkylbenzene type to assure miscibility. R-401A works fine provided compressor oil is changed.

R-124/152a/22 61/11/28

This is DuPont SUVA MP-66, or R-401B. The same comments for R-401A

15 apply here as well.

R-124/152a/22 33/15/32

This is DuPont SUVA® MP-52, or R-401C. The same comments for R-401A apply here as well.

R-600/124/134a 2/39/59

20 This is Intermagnetics General Corporation (IGC) FRIGC™ FR-12™. See U.S. Patent No. 5,425,890. FRIGC™ FR-12™ claims to be a "drop-in" for R-12, but the temperature-pressure curve is about 8 degrees Fahrenheit too low at evaporator temperatures (32 degrees Fahrenheit) in automotive air conditioning systems, causing low capacity, excessive compressor cycling and rapidly wearing out compressor clutches. Excessive clutch cycling may be eliminated by replacing low pressure cutout switches. FRIGC™ FR-12™ has poor mineral oil miscibility. FRIGC™ FR-12™ may become weakly or

-10-

highly flammable due to vapor leakage under cold (about 10 to about 25 degrees Fahrenheit) ambient conditions. However, the amount of flammable mass remaining would be small, in the order of 10 weight percent of the original system charge.

5 R-22/152a/142b/C318 45/7/5.5/42.5

This is China Sun G2015, or R-405A. R-405A has very marginal mineral oil miscibility, all components are totally immiscible with mineral oil except for R-142b and R-22, which are poor. The R-C318 component is expensive and the R-405A mixture was banned (listed as SNAP unacceptable) by the US EPA due to global warming concerns of the R-C318 component, which does not easily break down in the atmosphere, even after several thousand years.

10 R-22/218/142b 70/5/25

This is R-412A. Although intended as a "drop-in" substitute for R-500, it still has a temperature-pressure curve which is too high for most uses and limited 15 mineral oil miscibility, but slightly better miscibility than Forane® FX-56 and Forane® FX-57 due to more R-142b component. R-218 component is a perfluorinated fluorocarbon with a high global warming potential and a very long atmospheric lifetime, and like R-C318, the US EPA is not approving these compounds for refrigerants.

20 R-290/600a 60/40

Excellent refrigerant, with excellent oil miscibility. Low cost of components. The problem is the extreme flammability of all components (all hydrocarbons). Blends similar to this have been around a number of years. OZ-12, HC-12a, and ES-12r are tradenames of some similar hydrocarbon blends. At least 25 14 states have banned the use of hydrocarbon blends for motor vehicle air conditioning along with a Federal ban by the US EPA, which took effect on 7/14/95.

-11-

R-22B1 100

This is Bromodifluoromethane, or Great Lakes Chemical FM-100. The temperature-pressure curve is too low. R-22B1 boils at 4.2 degrees Fahrenheit (R-12 boils at -21.6 degrees Fahrenheit). R-22B1 contains a bromine atom, causing a significant ozone depletion potential, therefore the EPA will not approve its use for refrigerant. R-22B1 has excellent mineral oil miscibility.

R-134a 100

R-134a has complete immiscibility in mineral oil, making it not suitable for most R-12 applications. However, some systems, such as some household refrigerators, may successfully operate using R-134a in mineral oil if the pipe sizes are small enough to generate high enough gas velocities to drag the mineral oil around the refrigeration circuit. The compressor is usually located downhill from the evaporator, further minimizing oil return problems with an immiscible oil/refrigerant mixture.

R-152a/22B177/23

Good miscibility with mineral oil, but the temperature-pressure curve is too low. Both components have boiling points well above that of R-12. This mixture may be flammable if vapor leaked at temperatures below about 0 degrees Fahrenheit. R-22B1 is not approved by the US EPA for refrigerant use due to high ozone depletion potential.

R-227ea 100

No miscibility with mineral oil and the temperature-pressure curve is much too low.

25 R-152a/227ea 80/20

No miscibility with mineral oil and the temperature-pressure curve is lower than R-12, causing around a 10 percent reduction in capacity in unmodified

-12-

systems. This mixture will be flammable, especially when leaking at colder temperatures, below about 0 degrees Fahrenheit.

R-152a/227ea 50/50

No miscibility with mineral oil and the temperature-pressure curve is lower than R-12, causing around a 12 percent to 15 percent reduction in capacity in unmodified systems. This mixture may be flammable, especially when leaking at colder temperatures, below about 0 degrees Fahrenheit.

R-290/227ea 50/50

Good miscibility with mineral oil. Pressure-temperature curve is much too high, almost as high R-22. This mixture will be highly flammable.

R-152a 100

Flammable, but not as bad as propane (R-290). No miscibility with mineral oil. Temperature-pressure curve is too low, causing around a 10 percent reduction in capacity.

15 R-290/227ea 10/90

Good temperature-pressure curve, and good mineral oil miscibility. This blend will be flammable when vapor leaked at temperatures below about 0 degrees Fahrenheit and may be weakly flammable when leaked at higher temperatures. This mixture has a large mass fraction in the higher boiling component (R-227ea), which on some systems may cause unwanted liquid refrigerant return (slugging) to the compressor since there will be a large fraction of the boiling liquid near the exit end of the evaporator. This narrows the margins for charging and suction superheat setup on refrigeration systems.

25 R-227ea/E170 70/30

R-E170 is dimethyl ether. This mixture has good mineral oil miscibility, but the temperature-pressure curve is too low. This mixture may be flammable.

especially when vapor leaking at colder temperatures, such as below about 0 degrees Fahrenheit.

R-227ea/600a 75/25

Good mineral oil miscibility, but the temperature-pressure curve is way too low. This mixture might exhibit a region of flammability when vapor leaked in a temperature range of about 0 degrees Fahrenheit and about 100 degrees Fahrenheit.

R-152a/227ea 20/80

No mineral oil miscibility, and the temperature-pressure curve is too low. This mixture is probably non flammable or possibly weakly flammable over limited regions.

R-152a/13I1 25/75

R-13I1 is trifluoriodomethane (CF₃I). Pressure-temperature curve is too low. This mixture has a boiling point of about -8.5 degrees Fahrenheit. There are also concerns of the stability of R-13I1 due to the weakness of the iodine bond. The inventors of this mixture claimed that light broke down R-13I1 and caused refrigerant sight glasses to show purple in about two weeks. The inventors also claimed an extremely high ozone depletion potential for R-13I1, but an almost zero ozone depletion potential after release into the atmosphere after a small number of days (less than a week) due to the breakdown of the CF₃I molecule. Toxicity of CF₃I is not well established yet.

R-152a/227ea 25/75

No miscibility in mineral oil. The boiling point of -5.2 degrees Fahrenheit indicates a temperature-pressure curve which is too low. This mixture may also exhibit regions of flammability when vapor leaked at colder temperatures, below about 10 degrees Fahrenheit.

- 14 -

R-218/134a/600a 9/88/3

This is Isceon 49. Based on a published bubble point of 99 PSIA, the temperature-pressure curve may be a little high, but useable. R-218, a PFC,

5 is now banned by the US EPA for use in refrigerants due to high global warming potential and extremely long atmospheric lifetimes in the thousands of years. Mineral oil miscibility is very poor.

R-22/142b 40/60

Temperature-pressure curve is too low (R-22/142b 55/45 is much closer).

Vapor leaking may cause mixture to become weakly flammable, but with no

10 flashpoint. Mineral oil miscibility is poor, but may be useable in high temperature equipment (35 degrees Fahrenheit and higher) for the evaporator temperatures. Mineral oil miscibility is similar to (slightly better than) R-22.

R-134a/600a 80/20

15 Proposed by Electrolux. Good mineral oil miscibility, but the temperature-pressure curve appears to be slightly high from computer simulations (REFPROP V4.0) and almost azeotropic behavior is exhibited. This mixture appears to have a simulated boiling point about -28 degrees Fahrenheit. It may be a useable substitute for R-500 though. Some azeotropes exhibit a
20 boiling point outside the range (usually lower) of the boiling points of the individual components. The simulated azeotropy point is R-134a/600a 77.83/22.17 for this mixture. An azeotropic mixture behaves, for practical purposes over the temperatures of interest, as a single component refrigerant fluid. During the boiling of the liquid phase of the mixture, all components
25 evaporate at equal rates and fractionation does not occur. The glide is essentially zero. The simulated critical temperature is 211.0 degrees Fahrenheit, which is lower than that of R-134a, which will cause high head pressures in hot environments. This mixture will be flammable.

R-134a/152a 85/15

Boiling points of both components are lower than R-12. Temperature-pressure curve will be slightly too low at evaporator temperatures, but it closely matches that of R-134a (by computer simulation). Azeotropic behavior is observed from simulation, with boiling point of -15.62 degrees Fahrenheit which is practically the same as R-134a. No miscibility with mineral oil. This mixture should be nonflammable or weakly flammable at worst at temperatures of interest, but may be flammable under new strict US flammability standards such as Underwriters Laboratories (UL) 2182 where testing is currently performed at 100 degrees Centigrade.

R-134a/600a 95/5

Mediocre miscibility in mineral oils. The temperature-pressure curve is good (near azeotrope). This mixture should work fine in systems where the compressor does very little "oil pumping" (circulating oil in the refrigerant circuit), such as some household refrigerators. Other systems, especially automotive air conditioner compressors and commercial systems can circulate as much as 10 or 15 percent by volume of oil with the refrigerant. This mixture will not be able to return all the oil under those conditions. R-134a has zero oil miscibility by itself, and the addition of a small percentage of a hydrocarbon such as R-600a will not cause the R-134a itself to carry any oil and all the oil will have to be carried by the hydrocarbon. Flammability constraints limit the amount of the hydrocarbon component to around 5 percent.

Five pounds of the R-134a/600a 95/5 mixture were made up for test purposes. About two pounds were charged into the oil miscibility test stand described in Appendix A. Running the evaporator at about -40 degrees Fahrenheit for about 3 hours, caused severe oil return problems, with oil logging observed, and the crankcase oil level dropping. The evaporator temperature was raised to about 5 degrees Fahrenheit by partially closing

-16-

the manual evaporator pressure regulator valve, and oil continued to become trapped in the evaporator with further observed dropping of the crankcase oil level to near the bottom of the sight glass (compressor running, oil level at top of sight glass at start of run). No oil return was observed at either

5 temperature in the overhead suction line sight glass.

The evaporator temperature was then raised to about 30 degrees Fahrenheit, by the application of about 2500 watts of electrical power to the evaporator. A limited amount of oil was now observed returning to the compressor, as small (amount 1 mm in size) entrained "balls" in the suction gas flow. It was not creeping along the walls of the suction pipes as is usually the case with a mineral oil miscible refrigerant. It can therefore be concluded, that the addition of about 5 percent weight of isobutane to R-134a, provides only very limited mineral oil return capability, for high temperature systems, and is essentially useless for returning oil at lower temperatures of

15 operation. The oil used was Suniso 3GS (150 viscosity).

Since automotive compressor oil has a much higher viscosity than do most oils used for stationary refrigeration (automotive is usually 525 viscosity), the increase in oil return, due to the addition of the isobutane for automotive air conditioning, is expected to be almost nil.

20 The R-134a/600a 95/5 mixture should be nonflammable at normal temperatures of operation, but may be flammable under new strict US flammability standards such as Underwriters Labs (UL) 2182 where testing is currently performed at 100 degrees Centigrade.

R-218/152a 83.5/16.5

25 Claims to replace R-12, R-502, and R-22. This composition calculates (with REFPROP V4.0) computer simulation to have a temperature-pressure curve much too high for R-12 replacement. It is closer to R-22. Even if the R-218 weight percentage were drastically reduced and the R-152a increased to

achieve a good temperature-pressure curve for R-12, this mixture would still have no mineral oil miscibility. The R-218 is currently banned for refrigerants by the US EPA due to high global warming potential and long atmospheric lifetime.

5 R-22/142b/600a 55/41/4

This is R-406A, and it has performed satisfactorily in the field as a "drop-in" substitute for R-12, and it is nonflammable (after fractionating from vapor leaking) when used by those skilled in the art of refrigeration at normal temperatures of operation of R-12 refrigeration and air conditioning systems.

10 Safety testing by several independent labs has verified this. However, new very strict flammability regulations are coming into place in the United States, while other countries (many in Europe) are changing over to highly flammable hydrocarbon mixtures of refrigerants. Many refrigerant fluids will be essentially nonflammable at normal temperatures of operation, but may fail a
15 flammability test that specifies an artificially high temperature of operation such as 212 degrees Fahrenheit or higher. R-406A falls into this category.

It is clear from the foregoing discussion that a "drop-in" substitute for R-12, which does not require oil changes and has a higher critical temperature than R-134a, would result in many benefits.

20 The automotive air conditioning market for a R-12 substitute in the U.S. is huge with an estimated 125 million cars presently left using R-12. It is imperative that "drop-in" R-12 substitutes continue to be developed and used to prevent the costly and premature replacement of billions of dollars worth of refrigeration and air conditioning equipment.

SUMMARY OF THE INVENTION

In summary, I have discovered a group of refrigerant fluids, which are listed in Tables 1-3, which may be combined in novel ways to produce several excellent "drop-in" substitutes for refrigerants R-12 or R-500. The 5 performance of the preferred "drop-in" substitutes for R-12 or R-500 of the present invention often exceeds that of the refrigerant being replaced, while maintaining acceptable oil circulation with existing mineral oils used in R-12 or R-500 refrigeration and air conditioning systems. For the purposes of this invention, "refrigeration and air conditioning systems" will be referred to 10 collectively as "refrigeration systems." Also, for the purposes of this invention, "R-500 refrigeration systems" will be considered to be included within the phrase "dichlorodifluoromethane refrigeration systems."

One embodiment of the present invention is an improvement to the novel ternary mixture of refrigerants described in U.S. Patent No. 5,151,207, 15 which is a "drop-in" substitute for R-12, but unlike R-12, provides very little stratospheric ozone damage. One embodiment of the invention described in U.S. Patent No. 5,151,207 comprises a ternary mixture of refrigerants that is a "drop-in" substitute for dichlorodifluoromethane (R-12), comprising about 2 to 20 weight percent isobutane (R-600a), about 21 to 51 weight percent 20 chlorodifluoroethane (R-142b), and about 41 to 71 weight percent chlorodifluoromethane (R-22), with the weight percentages of the components being weight percentages of the overall mixture. One embodiment of the present invention improves on the invention of U.S. Patent No. 5,151,207, by 25 adding to the preferred embodiments disclosed therein one or more components from Tables 1 or 2.

Among the most preferred embodiments of the present invention are mixtures of refrigerants which are "drop-in" substitutes for

dichlorodifluoromethane (R-12), comprising about 0.5 to 8 weight percent isobutane (R-600a), about 15 to 60 weight percent of component B, and about 21 to 71 weight percent chlorodifluoromethane (R-22), with the weight percentages of the components being weight percentages of the overall mixture. Component B is about 1 to 99 weight percent chlorodifluoroethane (R-142b) and about 1 to 99 weight percent component C, with the weight percentages of the subcomponents of component B being weight percentages of component B. Component C is about 0 to 100 weight percent heptafluoropropane (R-227ea) and about 0 to 100 weight percent 10 chlorotetrafluoroethane (R-124), with the weight percentages of the subcomponents of component C being the weight percentages of component C.

Another embodiment of the present invention is the creation of additional "drop-in" substitutes for R-12 from novel mixtures of components 15 from Tables 1 - 3.

Another embodiment of the present invention is the creation of a "drop-in" or near "drop-in" substitute for R-500 from novel mixtures of components from Tables 1 - 3.

It is also an object of the present invention to provide a "drop-in" 20 refrigerant substitute for R-12 that provides an acceptable level of cooling in low, medium, and high temperature applications where R-12 is now in use, and that mixes well enough with compressor oils that are miscible with R-12 to provide adequate lubrication of existing compressors that utilize R-12. The mixing with existing R-12 oils must be sufficient to allow said oils to properly 25 circulate through the refrigeration circuit and not become excessively trapped (or "logged" in the refrigeration trade) in the evaporator, condenser or other parts of the system. Excessively trapped oils in the refrigeration circuit can

-20-

interfere with proper operation and efficiency of refrigeration systems, or in severe cases, cause compressor failure from lack of oil.

It is also an object of the present invention to provide additional flammability suppression in R-12 systems at elevated temperatures.

- 5 It is also an object of the present invention to provide a "drop-in" substitute refrigerant for R-12 that causes very little stratospheric ozone damage.

- 10 It is also an object of the present invention to provide a "drop-in" or near "drop-in" refrigerant substitute for R-500 that provides an acceptable level of cooling in low, medium, and high temperature applications where R-500 is now in use, and that mixes well with compressor oils that are miscible with R-500 to provide adequate lubrication of existing compressors that utilize R-500. The mixing with existing R-500 oils must be sufficient to allow said oils to properly circulate through the refrigeration circuit and not be excessively trapped (or "logged" in the refrigeration trade) in the evaporator, condenser or other parts of the system. Excessively trapped oils in the refrigeration circuit can interfere with proper operation and efficiency of refrigeration systems, or in severe cases, cause compressor failure from lack of oil.

- 15 It is also an object of the present invention to provide a "drop-in" or near "drop-in" refrigerant substitute for R-500 that provides an acceptable level of cooling in low, medium, and high temperature applications where R-500 is now in use, and that mixes well with compressor oils that are miscible with R-500 to provide adequate lubrication of existing compressors that utilize R-500. The mixing with existing R-500 oils must be sufficient to allow said oils to properly circulate through the refrigeration circuit and not be excessively trapped (or "logged" in the refrigeration trade) in the evaporator, condenser or other parts of the system. Excessively trapped oils in the refrigeration circuit can interfere with proper operation and efficiency of refrigeration systems, or in severe cases, cause compressor failure from lack of oil.

- 20 It is also an object of the present invention to provide a "drop-in" or near "drop-in" refrigerant substitute for R-500 that provides an acceptable level of cooling in low, medium, and high temperature applications where R-500 is now in use, and that mixes well with compressor oils that are miscible with R-500 to provide adequate lubrication of existing compressors that utilize R-500. The mixing with existing R-500 oils must be sufficient to allow said oils to properly circulate through the refrigeration circuit and not be excessively trapped (or "logged" in the refrigeration trade) in the evaporator, condenser or other parts of the system. Excessively trapped oils in the refrigeration circuit can interfere with proper operation and efficiency of refrigeration systems, or in severe cases, cause compressor failure from lack of oil.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to the embodiments described below and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations and further modifications in the described embodiments, and such further applications of the principles of the invention as described therein being contemplated as would normally occur to one skilled in the art to which this invention relates.

Since the January 7, 1991, filing date of the application which became U.S. Patent No. 5,151,207, several new refrigerant fluids which are listed in Table 1, below, have become available in commercial quantities. Refrigerant fluids that were referenced in U.S. Patent No. 5,151,207 are included in Table 2 for completeness. Additional known refrigerant fluids that are useful as mixture components in the present invention are also included in Table 3. Boiling points (BP), and critical temperatures (Crit) in Tables 1-3 are in degrees Fahrenheit and are taken from the November 1993 "NIST Database 23: NIST REFPROP v4.0", available from U.S. Department of Commerce, Technology Administration, National Institute of Standards and Technology (NIST), Standard Reference Data Program, Gaithersburg MD 20899, and the "June 1995 ARTI Refrigerant Database", available from Engineering Consultant, 10887 Woodleaf Lane, Great Falls VA 22066-3003. Molecular weights (MW) are taken from the same sources.

-22-

Table 1

R-num	Formula	Name	BP	Crit	MW
R-227ea	CF ₃ CHFCF ₃	1,1,1,2,3,3,3-heptafluoropropane*	2.5	215.37	170.0
R-124	CHClFCF ₃	2-chloro-1,1,1,2-tetrafluoroethane	8.26	252.45	136.4
R-134a	CF ₃ -CH ₂ F	1,1,1,2-tetrafluoroethane	-15.07	214.07	102.0
R-143a	CF ₃ -CH ₃	1,1,1-trifluoroethane	-53.23	163.58	84.04
R-125	C ₂ HF ₅	pentafluoroethane	-55.43	151.12	120.0
R-E125	CFH ₂ -O-CF ₃	difluoromethyltrifluoromethyl ether	-41.9	176.7	136.0
R-E143a	CH ₃ -O-CF ₃	methyl trifluoromethyl ether	-10.8	220.8	220.8
R-E227ca2	CHF ₂ -CF ₂ -O-CF ₃	1-(trifluoromethoxy)-1,1,2,2-tetrafluoroethane	26.3	186.0	238.3
R-245cb	CH ₃ -CF ₂ -CF ₃	1,1,1,2,2-pentafluoropropane	0.3	224.5	134.0

*At the present time, only the 1,1,1,2,3,3,3-heptafluoropropane isomer is available in commercial quantities, however, all isomers of heptafluoropropane are within the scope of the present invention.

Table 2

R-number	Formula	Name	BP	Crit	MW
R-600a	C(CH ₃) ₃	isobutane	10.83	274.46	58.12
R-142b	CF ₂ Cl-CH ₃	1-chloro-1,1-difluoroethane	15.55	278.87	100.4
R-22	CHF ₂ Cl	chlorodifluoromethane	-41.55	207.07	86.47

Table 3

R-num	Formula	Name	BP	Crit	MW
R-290	C3H8	propane	-43.75	206.06	44.10
R-E170	CH3-O-CH3	dimethyl ether (DME)	-12.7	263.8	46.07
R-1270	CH3CH=CH2	propylene	-53.8	198.4	42.07
R-1216	CF2=CFCF3	hexafluoropropene	-20.2	unknown	150.0
R-218	C3F8	perfluoropropane	-34.15	161.4	188.0
R-C318	C4F8	octafluorocyclobutane	19.42	239.6	200.4
R-C270	C3H6	cyclopropane	-27.2	256.3	42.1

10 The refrigerant fluids in Tables 1,2 and 3, may be grouped into four categories, GROUP-A, GROUP-B, GROUP-C, and GROUP-D as set forth in Table 4.. GROUP-A contains refrigerant fluids with the higher boiling points, GROUP-B contains refrigerant fluids which improve oil miscibility with R-12 mineral oils. GROUP-C contains refrigerant fluids with the lowest boiling points. GROUP-D refrigerant fluids may be used to dilute the other three groups. Some refrigerant fluids (e.g. R-142b) may be in more than one GROUP. Flammability is listed as "very" for very flammable refrigerant fluids, "weak" for weakly or mildly flammable refrigerant fluids and "none" for nonflammable refrigerant fluids. Miscibility of the refrigerant fluid with mineral oils used in R-12 refrigeration systems at a temperature range of about -20 degrees Fahrenheit to about 0 degrees Fahrenheit is listed as "none" for no oil miscibility, as "poor" for very limited oil miscibility, as "medi" for mediocre oil miscibility, and as "good" for complete oil miscibility. Oil miscibility with a given refrigerant fluid will improve with increasing temperature if the miscibility is listed as "poor" or "medi". The term "unkn" means "unknown".

15

20

25

-24-

Table 4

GROUP-A			GROUP-B			GROUP-C			GROUP-D		
Refrig	Flam	Oil	Refrig	Fla	Oil	Refrig	Flam	Oil	Refrig	Flam	Oil
R-227ea	none	none	R-142b	weak	medi	R-22	none	poor	R-134a	none	none
R-124	none	poor	R-600a	very	good	R-125	none	none	R-1216	none	none
R-142b	weak	medi	R-290	very	good	R-143a	weak	none			
R-F143a	unkn	good	R-F143a	unkn	good	R-F125	none	unkn			
R-E227ca2	none	unkn	R-F170	very	good	R-218	none	none			
R-245ch	unkn	unkn	R-1270	very	good						
R-C318	none	none	R-C270	very	good						

Preferred embodiments of the present invention include a mixture of refrigerant fluids with one or more components from GROUP-A, zero or more components from GROUP-B, one or more components from GROUP-C, and zero or more components from GROUP-D, subject to the three following conditions.

Condition 1. The resulting temperature versus pressure curve of a closed container containing said mixture of refrigerant fluids, such that all component refrigerant fluids coexist in both liquid and vapor states in the container, should approximate the temperature-pressure curve of a closed container of R-12 for the range of temperatures and pressures commonly used for R-12 refrigerant, about -40 degrees Fahrenheit to about 200 degrees Fahrenheit. The degree of approximation should be within about 15 percent to about 30 percent error. To account for the "glide" in the mixtures of refrigerant fluids,

the "bubble point" pressure at a temperature of 70 degrees Fahrenheit should be around 10 percent higher than the pressure (gauge pressure, PSIG) of R-12. Increasing the mass fraction of components from GROUP-C and decreasing the mass fraction of components from GROUP-A will cause 5 the pressure versus temperature curve of the mixture of refrigerant fluids to increase and vice versa. Rarely, two or more refrigerant fluids may be combined and the resultant boiling/bubble point of the mixture may not lie in between the boiling points of the components. This is the result of a partial or complete azeotrope formation. If an azeotrope is formed, the resultant 10 boiling/bubble point is often near or a few degrees lower than the component with the lowest boiling point. If an unwanted azeotrope forms, additional components can be added to further modify the temperature-pressure curve.

If the object is to produce a "high performance" or "higher capacity" mixture of refrigerant fluids, which may only be usable under certain 15 conditions, such as automotive air conditioning, where extra horsepower is available for compressor operation, or in low temperature situations where the compressor is under loaded, then the mass fraction of the components from GROUP-C may be further increased about 5 to about 20 weight percent. Conversely, to produce a "reduced capacity" mixture of refrigerant fluids, the 20 mass fraction of GROUP-C components may be reduced by about 5 to about 15 weight percent. Reduced capacity refrigerant mixtures will often perform poorly (but still useable) in "normal" systems. Air conditioning systems which were oversized when installed, may use a reduced capacity refrigerant to obtain a better equipment load match to the heat load. Properly sized air 25 conditioning systems provide far better humidity control (longer run times) than do oversized systems.

Condition 2. The resulting miscibility of mineral oils used in R-12 refrigeration systems with the mixture of refrigerant fluids created shall be great enough to provide for adequate circulation of said oils throughout the refrigeration circuit

without undue trapping or "logging" of said oils in any part of the system as to not interfere with the proper operation of the refrigeration system in the range of desired temperatures. Increasing the mass fraction of components from GROUP-B in the mixture of refrigerant fluids will increase miscibility with R-12 compressor oils at a given temperature and vice-versa.

In general, about 4 to 5 weight percent (of the total refrigerant mixture) of highly flammable GROUP-B components seem to provide usable mineral oil return in most cases, especially when combined with other weakly flammable GROUP-B components. Highly flammable GROUP-B components can usually be increased to about 8 to about 10 weight percent if weak flammability can be tolerated. Lowering the highly flammable GROUP-B components to as low as about 1 weight percent of the total refrigerant mixture will compromise mineral oil miscibility, but will often result in a refrigerant which is useful under some conditions, such as high temperature air conditioning or household refrigerators which can tolerate poor oil return.

Condition 3. The resulting mixture of refrigerant fluids should be nonflammable or weakly flammable at worst. The maximum mass fraction of "very" flammable refrigerant fluid components will be limited to about 5 to about 10 percent. The maximum mass fraction of "weakly" flammable

refrigerant fluid components will be limited to about 15 to about 60 percent. A test sample of the mixture of refrigerant fluids should be vapor leaked (fractionated) at several constant temperatures over the range of expected temperatures where the leaking may occur. Some temperatures for fractionation testing would typically be -20, 0, 40, 70, 120, 180 degrees Fahrenheit. Flammability tests should be conducted on the mass fractions of vapor and liquid phases and be analyzed with appropriate equipment (e.g. a gas chromatograph) at various points during each leak down to verify the mass fraction of flammable components does not become great enough to cause greater than "no" or "weak" flammability as desired. Flammability can

also be reduced by placing the boiling point of a very or weakly flammable refrigerant fluid near a lesser flammable or nonflammable refrigerant fluid component with a similar boiling point. Total flammability may also be reduced by spreading out (by boiling point) the flammable components over 5 the entire blend instead of using just one flammable component.

For the purposes of making the mixture of refrigerants of the preferred embodiments of the present invention, one needs to procure the following equipment, or equivalents. A mixing cylinder, which can be a standard refrigeration industry "recovery" cylinder or a small propane (20 pounds net 10 weight propane) tank is needed. These are U.S. Department of Transportation (DOT) rated at 240 PSIG or higher. This tank (or cylinder) must be clean. Also needed is a refrigeration (or equivalent) vacuum pump, scales, and a refrigeration manifold set (hoses and gauges).

The air must be removed from the mixing cylinder with a vacuum 15 pump, such as any used by refrigeration service technicians. A deep vacuum gauge is needed to verify that about a 200 micron vacuum is achieved on the mixing cylinder. Deep vacuum gauges which read to less than 25 microns are commonly available at refrigeration supply houses.

This mixing cylinder is placed on electronic charging scales, of the type 20 commonly available to the refrigeration service technician. These scales often read in 1/2 ounce increments up to a total of 60 pounds or more total weight.

A refrigerant mixture is made, by connecting up each component 25 supply cylinder to the mixing cylinder on scales, and weighing in the appropriate weight percentage of each component. The mixing hoses or manifolds should be purged or evacuated first to remove air and moisture. Each component supply cylinder should have a "dip tube" or eductor tube to withdraw the component in liquid phase. If the supply component cylinder

-28-

does not have a dip tube, it must be inverted to obtain the component in liquid phase.

Although, the components can be mixed in any order, it is easier to add the high boiling components first. The vacuum on the cylinder will usually be sufficient to draw in the required amount of the first component.

5 Some sort of liquid pump will be required to transfer the remaining GROUP-A and GROUP-B components as the pressure on the mixing cylinder will rise to match the supply cylinder.

10 Instead of a liquid pump, the mixing cylinder may be chilled by any convenient means by 10-20 degrees Fahrenheit colder than the supply cylinders. Alternately, the component supply cylinder may be heated 10-20 degrees Fahrenheit warmer than the mixing cylinder to facilitate the transfer. A hot water bath or cylinder heating blanket works nicely for this purpose.

15 When transferring GROUP-C components, no pump will be needed, as the higher pressures of GROUP-C components will (rapidly) transfer them to the mixing cylinder. Caution is advised, for after the relatively slow transfers for GROUP-A and GROUP-B components into the mixing cylinder, GROUP-C components will transfer very quickly, possibly surprising the person doing the mixing, and causing too much of a component to be transferred.

20 A refrigerant mixture, just completed, should be allowed to thermally stabilize or 12 hours or more before temperature and pressure measurements are taken, if needed. If static pressure and temperature measurements are not needed, a mixture may be charged into a refrigeration or air conditioning system and operated, without the 12 hour or more delay. A refrigerant mixture should always be unloaded from the mixing cylinder in liquid phase when charging into an appliance or other refrigeration system. This prevents fractionation from changing the composition of the mixture during charging.

The mixing cylinder may contain a "dip tube" to provide for unloading in liquid phase. If a mixing cylinder is used without a dip tube, the cylinder must be inverted to unload in liquid phase.

5 If a mixture contains significant mass fractions of components with high molecular mass, the molecular mass of the total refrigerant mixture will increase. This may be beneficial for operation in centrifugal chiller refrigeration systems.

10 Extensive use of R-406A, described by U.S. Patent No. 5,151,207, shows the mixture of refrigerants to be zeotropic, which means the composition changes during evaporation and condensation phases of refrigeration or air conditioning system operation. Unlike a single component refrigerant, such as R-12, zeotropic refrigerants do not evaporate or condense at a single temperature (for a given pressure), but they evaporate or condense over a small range or "glide" of temperatures. Depending on the 15 temperature, the glides involved for both R-406A and the preferred embodiments of the present invention are in the order of 10 to 15 degrees Fahrenheit.

20 Some refrigeration systems have seen performance improvements upwards of about 30 to about 40 percent due to the glide factor. Other systems exhibit similar performance to that of R-12. Events taking place in the condenser are broken down into 3 rough areas. The hot gas upon entering the condenser is first desuperheated, no condensation takes place in this area, just a relatively low amount of heat is rejected in cooling the hot gas down to the point where it is ready to condense. The second area involves 25 the actual condensation of the gas, where a phase change occurs to liquid state. A relatively high amount of heat is given off due to the phase change. Thirdly, the now liquid refrigerant is further cooled (called subcooling in the art), with a relatively low amount of heat rejected.

-30-

Zeotropic mixtures, such as those of the present invention, cause the condensation phase change area (and evaporation phase change area) to occupy more of the condenser (or evaporator), thus increasing the capacity of the condenser to reject or the evaporator to gain heat.

5 Oil miscibility may be tested by mixing refrigerant and oil samples in a glass tube refrigerant charging cylinder, such as a "Dial-a-Charge" or a smaller device called a "Vizi-vapor" charging device that can hold 2 or 3 fluid ounces of refrigerant/oil mixtures. The sample is chilled to the desired temperature of operation and then observed for the oil separating from the refrigerant. Complete or almost complete separation is a sign that the oil and refrigerant may be immiscible at the sample temperature and oil return problems to the compressor might be expected. If the oil and refrigerant stay mixed or only separate only a small amount, then oil miscibility at the tested temperature is assured. If a large amount of separation is observed, further testing needs to be done, preferably in a real refrigeration system or refrigeration system test stand.

10

15

Oil miscibility can also be tested in a real system, by using a system with a compressor with an oil sight glass in the crankcase. Once the desired temperatures are reached, the oil level is observed, and if it drops, then it is probably not being returned from the evaporator, and a more miscible combination must be used. Sight glasses should also be present in critical areas of the system, where oil logging may occur (e.g., a low spot in the evaporator or the suction line) The few fluid ounces of oil needed to log an evaporator enough to interfere with system operation, may not cause an easily detectable loss of oil on the compressor crankcase sight glass due to all the foaming and churning in the crankcase from compressor operation, and hence the need to install sight glasses or other means of detecting oil logging in critical system areas.

20

25

Table 5 lists current ozone depletion potentials (ODPs) and global warming potentials (GWPs) of the components used in the following examples. ODP (ozone depletion potential) is calculated for mixtures by using June 1995 ARTI Refrigerant Database, reported ODPs of the individual component weight percentages. R-12 has an ODP of 1.0, the benchmark ODP. GWP (global warming potential) is calculated relative to CO₂, from the same source. Each following example will list calculated ODP (as ODP=) and GWP (as GWP=) for the mixture of that example.

Table 5

Refrigerant Fluid	ODP (100 year)	GWP (100 year to CO ₂)
R-12	1.0	7900
R-22	.050 (semi-empirical)	1700
R-142b	.066 (semi-empirical)	2000
R-124	.030 (model-derived)	480
R-227ea	.000	3300
R-E170	.000	0
R-600a	.000	0

Example 1 (a most preferred embodiment)

25 pounds of R-600a/142b/124/22 4/16.5/28.5/51 (ODP=.0449

GWP=1334), a "drop-in" substitute refrigerant for an R-12 automotive air conditioning system, were blended into a mixing cylinder (30 lb "disposable" DOT-39 cylinder manufactured by Worthington Cylinders) with a dip tube

-32-

using the methods and procedures described above. Flammability suppression was desirable and the higher evaporator temperatures in a car (32 degrees Fahrenheit and above) resulted in good oil miscibility, even with higher percentages of R-124 (lower percentages of R-142b). There was less 5 flammability suppression and more oil miscibility than in Example 2, below. The refrigerant mixture of this Example (minus the oil) has been found to be nonflammable, even after worst case vapor leakage (fractionation), at cold 10 temperatures (-10F range), with worst cases (highest concentrations of flammables) points tested for flammability at 100 degrees Centigrade with methods specified by Underwriters Laboratories (UL) standard 2182.

Two pounds of the refrigerant mixture of Example 1 were charged into the air-conditioning system of a 1990 Pontiac Transsport minivan.

Driving 35 mph at an ambient temperature of 80 degrees Fahrenheit, discharge air duct temperatures of 36 to 39 Fahrenheit were achieved.

15 Controls were set to "MAX" (recirculate) and the highest fan speed. Low side (suction) pressure was 30 PSIG (set by the GM-V5 variable displacement compressor), high side (head) pressure was 150 PSIG. Later in the day, when the ambient temperature fell to 75 degrees Fahrenheit, the head pressure dropped to 125 PSIG, and the duct temperature rose to 39 to 42 20 degrees Fahrenheit.

The Example 1 refrigerant mixture was also charged into several taxicab vehicles in Florida for a two month test, and the company reported back good results. Additional testing at a technical school in Florida in stationary equipment, showed nearly identical results to R-406A.

25 The Example 1 refrigerant mixture was run in an oil miscibility test stand, a real refrigeration system, described in appendix A. Evaporator and suction line sight glasses showed the refrigerant/oil mixtures becoming cloudy in the range of -25 to -30 degrees Fahrenheit, a sign that refrigerant/oil

miscibility is starting to be lost. The mineral oil used was Suniso 3GS 150 viscosity, the type commonly found in stationary R-12 refrigeration equipment. Oil return to the compressor was still acceptable after 48 hours of running at -40 degrees Fahrenheit on the evaporator.

5 Automotive compressor mineral oil, Suniso 5GS 525 viscosity, was also tested and found to go cloudy at around 15 degrees Fahrenheit. A 4 hour run showed this thicker oil still returned acceptably at around 5 degrees Fahrenheit. This is enough miscibility for automotive air conditioning systems, where evaporator temperatures are 25 degrees Fahrenheit or higher.

10 The Example 1 refrigerant mixture offers roughly 20 percent less ozone depletion and about 25 percent less global warming than does R-406A. Example 1 refrigerant mixture offers about 96 percent less ozone depletion and about 83 percent less global warming than R-12.

	R-600a/142b/124/22	4/16.5/28.5/51	ODP=.0449 GWP=1334 (Example 1)
15	R-600a/142b/22	4/41/55	ODP=.0546 GWP=1755 (R-406A for comparison)
	R-12 (pure)	100	ODP=1.000 GWP=7900 (R-12 for comparison)

Example 2

20 R-600a/142b/124/22 4/13/33/50, a "drop-in" substitute refrigerant mixture for an R-12 automotive air conditioning system, is created in the manner set forth in Example 1 above. Flammability suppression is desirable and the higher evaporator temperatures in a car (32 degrees Fahrenheit and above) results in good oil miscibility, even with higher percentages of R-124

-34-

(lower percentages of R-142b). The blend in this Example was computer simulated with NIST program REFPROP V4.0 and showed good results.

Compared to R-406A, the Example 2 refrigerant mixture offers about 20 percent lower ozone depletion and about 30 percent less global warming.

5 R-600a/142b/124/22 4/13/33/50 ODP=.043 GWP=1268 (Example 2)
R-600a/142b/22 4/41/55 ODP=.0546 GWP=1755 (R-406A for
comparison)

Example 3

10 R-600a/142b/124/22 4/34/7/55, a "drop-in" substitute for R-12 in a walk-in freezer, operating at -20 degrees Fahrenheit, is created in the manner set forth in Example 1 above. Due to the low evaporator temperature, oil miscibility is of paramount importance. A higher percentage of R-142b and a lower percentage of R-124 are used. Computer simulations showed good results.

15 The Example 3 refrigerant mixture offers about same ozone depletion and global warming as R-406A. Any weak flammability which might result from a vapor leak of R-406A under cold temperatures is reduced.

R-600a/142b/124/22 4/34/7/55 ODP=.052 GWP=1648 (Example 3)
R-600a/142b/22 4/41/55 ODP=.0546 GWP=1755 (R-406A for
20 comparison)

Example 4 (a most preferred embodiment)

R-600a/142b/227ea/22 4/15/40/41, a "drop-in" substitute refrigerant for an R-12 automotive air conditioning system, is created in the manner set forth in Example 1 above. A high percentage of R-227ea is used and some

flammability suppression is provided in the event of a collision where refrigerant lines are ruptured and compressor oil is sprayed onto hot exhaust manifolds or the catalytic converter. This mixture also has a lower ODP than other Examples. This refrigerant mixture has been computer simulated using

5 NIST REFPROP V4.0 and showed favorable results.

Example 4 offers almost one half the ozone depletion of R-406A (97 percent less ODP than R-12), however, the global warming potential is about 25 percent greater than R-406A.

R-600a/142b/227ea/22 4/15/40/41 ODP=.03 GWP=2317 (Example 4)

10 R-600a/142b/22 4/41/55 ODP=.0546 GWP=1755 (R-406A for comparison)

Two cylinders, each containing 25 pounds of the Example 4 refrigerant mixture, were made in the manner set forth above. About two pounds of the Example 4 refrigerant mixture were charged into the oil miscibility test stand described in Appendix A. Oil return to the compressor was slightly worse than for the refrigerant mixture of Example 1. Oil return was still adequate down into the -20 to -30 degree Fahrenheit range. Suniso 3GS (150 viscosity) mineral oil was used.

20 2.5 pounds of the Example 4 refrigerant mixture were charged into a Nor-Lake brand 4 door chest type cooler made for R-12 refrigerant. This unit is at least 30 years old and had been out of service (leaks and dirty condenser coil) for two years (R-12). The unit was first cleaned up and repaired and charged with R-406A refrigerant mixture to verify operation. The R-406A refrigerant mixture was removed before charging in the Example 25 4 refrigerant mixture. The cooler ran normally. Ambient temperature was about 78 degrees Fahrenheit, and upon initial startup, the head pressure was 148 PSIG, and the suction pressure was 40 PSIG. After sixteen minutes, the

-36-

unit had cooled down and cycled off, with the head pressure being 128 PSIG and the suction pressure being 21 PSIG at the end of the cycle.

Example 5

5 R-600a/142b/124/227ea/22 4/15/17/20/44, a "drop-in" substitute refrigerant for an R-12 automotive air conditioning system of the following mixture is created in the manner set forth in Example 1 above. More nonflammables are delivered at higher boiling points than Example 4 in the case of a system rupture. This mixture has been computer simulated using NIST REFPROP V4.0 with good results.

10 Example 5 is a compromise between Examples 1 and 4. Ozone depletion is reduced about one third R-406A with similar global warming to R-406A.

R-600a/142b/124/227ea/22 4/15/17/20/44 ODP=.037 GWP=1789
(Example 8)

15 R-600a/142b/22 4/41/55 ODP=.0546 GWP=1755 (R-406A for comparison)

Example 6

20 R-E170/142b/124/22 4/16.5/28.5/51 (ODP=.0449 GWP=1334), a "drop-in" substitute for R-12, was created in the manner set forth in Example 1, above. It is the same as Example 1, except that Dimethyl ether (R-E170) has been substituted for the isobutane (R-600a), which created an equivalent refrigerant. R-E170 has good mineral oil miscibility, as does isobutane. The temperature-pressure curve almost exactly matches that of Example 1 (See Figure 1).

25 A cylinder containing 25 pounds of the Example 6 refrigerant mixture was made in the manner set forth above. About 8 ounces (weight) of

-37-

Example 6 refrigerant mixture were charged into a Kelvinator model FDK190KNH2 household refrigerator. The refrigerator was started at room temperature (about 70 degrees Fahrenheit). After 30 minutes of operation, pressures, and the compressor Ampere draw were normal. Suction pressure was 2 PSIG, head pressure was 125 PSIG, and the compressor current draw was 2.2 Amperes (current draw with R-12 was also 2.2 Amperes). Inside 5 freezer compartment was 20 degrees Fahrenheit and the fresh food compartment was at 36 degrees Fahrenheit. However, the service technician noted that the condenser inlet was hotter to the touch than it would have been with R-12. This is due to the higher heat of compression of the R-22 component. R-406A exhibits slightly higher compressor discharge 10 temperatures than R-12 also. The slightly higher discharge temperatures are well within equipment operating capabilities and cause no problems. The "frost line" was at the end of the evaporator.

15

Example 7

4 pounds of the Example 6 refrigerant mixture were charged into the R-12 air conditioning system on a 1985 MACK "cab-over" semi tractor. The system performed identical to factory specifications for this system charged with R-12. Design suction pressure range was 18 to 25 PSIG (at 2000 RPM, 20 80 degrees Fahrenheit ambient), the system with the Example 6 refrigerant mixture ran at about 19 to 20 PSIG on the suction side. Design head pressure range (with R-12) is 250-275 PSIG with 260 PSIG being measured when operating on the Example 9 refrigerant mixture.

Example 8

25 A "Masterbuilt" brand chest type cooler was also charged with 9.0 ounces (weight) of the Example 6 refrigerant mixture. It used a thermostatic expansion valve (TEV) refrigerant metering device. After 15 minutes of operation, the suction pressure was 40 PSIG and the head pressure was 130

-38-

PSIG, with the food compartment temperature being 35 degrees Fahrenheit. Compressor current draw with the Example 6 refrigerant mixture was 1.8 Amperes (1.9 Amperes for R-12). The refrigerant sight glass was clear (no bubbles). The "frost line" was at the end of the evaporator.

5

Example 9

A Frige-Air brand display case model LKC2680 (TXV refrigerant metering device) was charged with 6 ounces (weight) of the Example 6 refrigerant mixture. The "pull down" (cool down until unit cycled off) for this unit was 18 minutes for both R-12 and the Example 6 refrigerant mixture.

10 The food compartment temperature at the end of the cool down time was 34 degrees Fahrenheit for the Example 9 refrigerant mixture and 40 degrees Fahrenheit for R-12. The refrigerant sight glass was clear (no bubbles) and the "frost line" was at the end of the evaporator. Compressor current draw as 1.9 Amperes for both the Example 6 refrigerant mixture and R-12. A higher
15 condenser inlet temperature (compressor discharge) was also observed by feel.

Additional refrigerant mixtures

Additional refrigerant mixtures are created in the manner set forth above from components in Tables 1-3 using Conditions 1-3. Some of the
20 mixtures may not be the best performers nor have the best mineral oil miscibility, but they should be functional in at least some types of R-12 refrigeration or airconditioning systems as a "drop-in" replacement for R-12.

Example 10

R-600a/124/134a/22 6/26/40/28

25 Poor oil miscibility, may only work for high temperature systems, such as cars. Dilution by R-134a also reduces the glide (and performance).

-39-

Example 11

R-227ea/22 75/25

Very poor oil miscibility, might work in some cars. Would work if oil was changed to alkylbenzene.

5

Example 12

R-124/142b/125 47/15/38

Poor oil miscibility, low critical temperature, may work in high temperature systems (cars). Temperature-pressure curve is OK. Low critical temperature may generate high head pressures and loss of performance in hot climates or
10 stopped traffic.

Example 13

R-600a/142b/124/22 1.5/9.5/39/50

Very good flammability suppression at elevated temperatures, but very poor miscibility in mineral oil. This will only be useful in high temperature air
15 conditioning systems, such as some cars, and household refrigerators which can tolerate almost zero mineral oil refrigerant miscibility. Certain cars, with compressors mounted higher than the evaporator and using a small oil charge may see oil starvation due to poor oil return.

Example 14

20 R-600a/142b/124/218 4/8/13/75

Low critical temperature, but will still perform better than R-134a. Good oil miscibility. The U.S. EPA currently takes a dim view of perfluorinated fluorocarbons (R-218) since they are so stable and do not easily break down in the atmosphere for thousands of years, adding to global warming. This
25 thinking might change in the future as more is learned about the global warming mechanisms.

-40-

Example 15

R-600a/124/134a/22 6/26/40/28

Improvement to FRIGC™ FR-12™, increase oil miscibility, and capacity. This mixture may work about the same as R-12 but not as good as a mixture with a higher glide, such as R-406A or a preferred embodiment of the present invention. This embodiment will have better oil miscibility than does FR-12™, but it is still very limited, and useful only for high temperature systems.

Examples 16-113

Additional refrigerant mixtures of the present invention of Examples 16-113 are summarized in Table 6, below. For completeness, Examples 1-15 are also included in Table 6. Most of the refrigerant mixtures in Table 6 were computer simulated with NIST program REFPROP V4.0 and showed good results. General comment(s) are included for each entry in Table 6. The "fig." column refers to the figure number containing the temperature-pressure chart for the blend. The word "oil" in Table 6 is meant to mean "mineral oil used in R-12 refrigeration and air conditioning systems". Oil miscibility (ability of the oil to correctly return to the compressor is given a letter "grade" of A to F defined as follows:

- A No problems with mineral oil return (150 viscosity) down to -50 degrees Fahrenheit or colder evaporator temperatures.
- B No problems with mineral oil (150 viscosity) return down to about -30 degrees Fahrenheit evaporator temperatures.
- C No problems with mineral oil (150 viscosity) return for most R-12 systems down to about -10 to about 10 degrees Fahrenheit. A small

number of systems may log oil or fail from poor oil return even at about 10 degrees Fahrenheit evaporator temperatures.

D Only usable in some systems, and only for "high temperature" (air conditioning, about 35 degrees Fahrenheit and warmer) use. Due to 5 small line sizes (high suction gas velocities), many R-12 household refrigerators would still be usable, but not R-12 "commercial refrigeration" systems.

F Total mineral oil immiscibility with the refrigerant. Only a very few systems, probably "household" refrigerators, would be able to operate correctly. Pure R-134a (in mineral oil) is a good example of "F". It is 10 outside the scope of the present invention to claim a refrigerant mixture with no miscibility in mineral oil, therefore, no examples are included with a mineral oil miscibility of "F" in Table 6, below.

Table 6

Example	Components	Composition	Oil	fig.	General comments
1	R-600a/142b/124/22	4/16.5/28.5/51	A-	1	preferred embodiment, best overall refrigerant
2	R-600a/142b/124/22	4/13/33/50	B+	2	slightly lower oil miscibility, better flammability suppression
3	R-600a/142b/124/22	4/34/7/55	A	2	might fractionate to slightly flammable (vapor leaking)
4	R-600a/142b/227ea/22	4/15/40/41	B	2	preferred embodiment, more costly, less oil misc than Example 1
5	R-600a/142b/124/227ea/22	4/15/17/20/44	B	2	combination of Example 1 and Example 4
6	R-E170/142b/124/22	4/16.5/28.5/51	A-		Equivalent to Example 1 except using R-E170 instead of R-600a
7 thru 9	same refrigerant as Example 6				
10	R-600a/124/134a/22	6/26/40/28	C-	2	reduced glide (dilution by 134a) compared to Example 1
11	R-227ea/22	75/25	D-	3	very bad oil misc, excellent fire suppression
12	R-124/142b/125	47/15/38	D	3	poor oil misc, glide too high
13	R-600a/142b/124/22	1.5/9.5/39/50	D+	3	good flammability suppression, but poor oil miscibility
14	R-600a/142b/124/218	4/8/13/75	C-	3	R-218 is PFC, currently banned by USEPA for refrigerants
15	R-600a/124/134a/22	6/26/40/28	C-	3	poor oil return, to D+ after vapor leaking
16	R-600a/124/134a/143a	6/40/26/28	D+	4	poor oil return
17	R-600a/124/134a/143a/125	6/40/26/14/14	D+	4	poor oil return
18	R-600a/124/134a/143a/125/121	6/40/16/14/14/10	A		weakly flammable, oil misc to D+ after vapor leaking
19	R-600a/124/134a/143a/290	3/44/26/24/3	D	4	poor oil return
20	R-600a/124/134a/290/22	3/40/26/3/28	D+	4	poor oil return

Table 6 Cont.

Example	Components	Composition	Oil	fig.	General comments
21	R-142b/E124/134a/290/22	15/15/26/4/40	B+	5	oil misc will degrade to C- or D+ after vapor leaking
22	R-E143a/E170/124/142b/22	5/5/28/12/50	B+		limited availability of R-E143a
23	R-227ea/E142b/22	40/20/40	D	5	expensive (227ea), poor oil misc
24	R-600a/E142b/124/22	4/14.5/20.5/6/1	B+	5	"high performance" version of Example 1 (higher pressures)
25	R-290/E142b/22	5/46/49	A	5	weakly flammable, oil misc to C after vapor leaking
26	R-290/E142b/22/600a	2/44/5/1/3	A	5	weakly flammable after vapor leaking
27	R-600a/E142b/124/22/290	4/16/32/44/4	A	6	good refrigerant, slight decrease in oil misc upon vapor leak to B+
28	R-600a/E142b/124/22/1270	4/16/33/43/4	A		good refrigerant, slight decrease in oil misc upon vapor leak to B+
29	R-600a/E142b/124/E125/290	4/16/33/43/4	A		good refrigerant, slight decrease in oil misc upon vapor leak to B+
30	R-600a/E142b/124/E125/1270	4/16/32/44/4	A		good refrigerant, slight decrease in oil misc upon vapor leak to B+
31	R-600a/E142b/125/290	4/48/43/4	A	6	weakly flammable after vapor leaking, high glide
32	R-600a/E142b/125/1270	4/50/42/4	A		weakly flammable after vapor leaking, high glide
33	R-600a/E142b/22/125/290	4/45/24/23/4	A	6	weakly flammable after vapor leaking, slightly higher glide
34	R-600a/E142b/22/125/1270	4/46/24/22/4	A	6	weakly flammable after vapor leaking, slightly higher glide
35	R-600a/E142b/134a/22/290	4/35/10/46/5	A	6	oil misc slight decrease to B+ on vapor leak, reduced glide
36	R-600a/E142b/134a/22/1270	4/36/10/45/5	A		oil misc slight decrease to B+ on vapor leak, reduced glide
37	R-600a/E24/22/290	4/52/40/4	B-	7	oil misc decrease to C- on vapor leaking
38	R-600a/E24/22/1270	4/53/39/4	B-		oil misc decrease to C- on vapor leaking
39	R-600a/E124/134a/22	4/37/20/39	D+	7	low glide, low oil misc.

Table 6 Cont.

Example	Components	Composition	oil	fig.	General comments
40	R-600a/227ea/22/290	4/65/27/4	B-	7	expensive (227ea), oil misc degrades to D+ after vapor leaking
41	R-600a/245cb/22/290	4/63/29/4	B-	7	expensive (245cb), oil misc degrades to D+ after vapor leaking
42	R-600a/227ea/22/290/134a	4/55/17/4/20	C+	7	expensive (227ea)
43	R-E170/600a/142b/22	2/24/15/5	A		weakly flammable after vapor leaking
44	R-600a/E170/142b/124/22	2/217/29/50	A-		equivalent to Example one, some R-600a replaced with R-E170
45	R-E170/142b/22/290	4/41/5/1/4	A+		might be weakly flammable, oil misc goes to A- vapor leaking
46	R-E170/142b/124/22/290	4/17/29/46/4	A		oil misc goes to A- after vapor leaking
47	R-E170/227ea/22	4/71/25	D		expensive (227ea), poor oil misc
48	R-E170/227ea/125/143a/290	4/54/20/18/4	C+		expensive (227ea), oil misc drops to C- after vapor leaking, 0 ODP
49	R-E170/227ea/134a/125/290	4/52/20/20/4	C+		expensive (227ea), oil misc drops to C- after vapor leaking, 0 ODP
50	R-600a/227ea/134a/143a/290	4/54/20/18/4	C+	8	expensive (227ea), oil misc drops to C- after vapor leaking, 0 ODP
51	R-600a/227ea/134a/125/290	4/52/20/20/4	C+	8	expensive (227ea), oil misc drops to C- after vapor leaking, 0 ODP

Table 6 Cont.

Example	components	Composition	Oil	fig.	General comments
52	R-E227ca2/600a/218/290	27/4/65/4	C-		oil goes to D- after vapor leaking, R-218 not EPA approved
53	R-C318/E170/218/290	28/4/64/4	C-		oil goes to D- after vapor leaking, R-C318, 218 not EPA approved
54	R-E227ca2/600a/218/1270	29/4/63/4	C-		oil goes to D- after vapor leaking, R-218 not EPA approved
55	R-600a/142b/E125	4/4/155	A		weakly flammable after vapor leaking
56	R-600a/142b/E125/290	2/4/155/2	A		weakly flammable, oil misc to B+ after vapor leaking
57	R-600a/142b/125	4/46/50	A		weakly flammable after vapor leaking, high glide
58	R-600a/142b/124/125	4/18/32/46	A-	8	similar to Example 1, but higher glide
59	R-600a/142b/124/125/290	4/18/32/42/4	A	9	oil goes to A- after vapor leaking
60	R-600a/227ea/125	4/69/27	D	9	expensive (227ea), poor oil misc, good glide, zero ODP
61	R-E170/227ea/125	4/69/27	D		expensive (227ea), poor oil misc, good glide, zero ODP
62	R-600a/124/134a/125/290	3/42/26/26/3	C-	9	oil misc will drop to D after vapor leaking
63	R-600a/142b/227ea/22	4/15/30/51	B	9	"high performance" version of Example 4 (higher pressures)
64	R-E170/142b/124/22	4/14.5/20.5/61	B+		"high performance" version of Example 8 (higher pressures)
65	R-600a/142b/124/22/290	4/16/22/54/4	A	9	"high performance" version of Example 30 (higher pressures)

Table 6 Cont.

66	R-600a/124/22/290	6/48/4/2/4	B+	10	oil misc drops to B- on vapor leaking
67	R-600a/124/125	8/51/4/1	B-	10	high glide
68	R-600a/124/22	8/45/4/7	B*	10	worse oil misc and lower critical temp than R-406A
69	R-600a/142b/124/22	3/18/24/5/5	B+	10	pressures between "normal" and "high performance" use
70	R-600a/124/125/280	6/54/36/4	B+	10	oil misc drops to B- on vapor leaking, higher glide than Ex. 66
71	R-E170/124/125	8/51/4/1	B-		high glide
72	R-E170/124/22	8/45/4/7	B		worse oil misc and lower critical temp than R-406A
73	R-E170/124/22/290	6/48/4/2/4	B+		oil misc drops to B- on vapor leaking
74	R-E170/124/125/290	6/54/36/4	B+		oil misc drops to B- on vapor leaking, high glide
75	R-600a/227ea/124/125	8/30/27/35	B	11	expensive (227ea)
76	R-600a/142b/227ea/124/125	5/16/22/18/39	B+	11	less expensive to make than Example 75
77	R-600a/142b/227ea/125	5/16/4/1/38	B+	11	expensive (227ea). Mol. weight may be high enough for chillers
78	R-600a/227ea/125/290	5/70/21/4	B+	11	expensive (227ea), low critical temp, high glide, zero ODP
79	R-E170/227ea/125/290	5/70/21/4	B+		expensive (227ea), low critical temp, high glide, zero ODP
80	R-E170/142b/125/290	4/49/43/4	A		weakly flammable
81	R-142b/125	53/4/7	D+	11	weakly flammable after vapor leaking, high glide
82	R-142b/125/290/134a	47/38/5/10	A	12	weakly flammable, oil drops to C-/D+ on vapor leaking
83	R-142b/125	43/5/7	D+	12	weakly flammable after vapor leaking, high glide, high performance

Table 6 Cont.

Example	components	Composition	oil	fig.	General comments
84	R-142b/125/290	52/43/5	A	12	weakly flammable, oil goes to C-/D+ after vapor leaking, high glide
85	R-142b/143a	57/43	D+	12	weakly flammable, high glide
86	R-600a/124/125/290	6/44/46/4	B+	12	high performance version of Example 70
87	R-124/143a	68/32	D-	13	very marginal mineral oil misc.
88	R-E170/227ea/143a	5/70/25	C-	zero ODP	
89	R-600a/227ea/143a	5/70/25	C-	13	zero ODP
90	R-600a/124/125/1270	6/55/35/4	B+	66	oil misc drops to B- on vapor leaking, higher glide than Ex. 66
91	R-E170/124/22/1270	6/49/41/4	B+		oil misc drops to B- on vapor leaking
92	R-E170/124/125/1270	6/55/35/4	B+		oil misc drops to B- on vapor leaking
93	R-600a/227ea/125/1270	5/71/20/4	B+		expensive (227ea), low critical temp, high glide, zero ODP
94	R-E170/227ea/125/1270	5/71/20/4	B+		expensive (227ea), low critical temp, high glide, zero ODP
95	R-E170/142b/125/1270	4/50/42/4	A		weakly flammable
96	R-142b/125/1270/134a	4/7/38/5/10	A		weakly flammable, oil misc drops to C-/D+ on vapor leaking
97	R-142b/125/1270	53/42/5	A		weakly flammable, oil goes to C-/D+ after vapor leaking, high glide
98	R-600a/142b/124/22	8/14.5/26.5/51	A+	13	Ex1 with more isobutane, weakly flammable, still usable
99	R-600a/142b/124/22	2/17.5/29.5/51	C	13	Ex1 with less R-600a, worse oil miscibility, usable in some systems

Table 6 Cont.

Example	components	Composition	oil	fig.	General comments
100	R-600a/142b/124/22	4/21.5/23.5/41	B	13	Ex1 with less R-22, lower pressures, usable in some systems
101	R-600a/142b/124/22	4/9/21/66	C+	14	Ex1 with more R-22, higher pressures, usable in some systems
102	R-600a/142b/227ea/22	8/13/38/41	A-	14	Ex4 with more isobutane, weakly flammable, still usable
103	R-600a/142b/227ea/22	2/16/4/141	C-	14	Ex4 with less R-600a, worse oil miscibility, usable in some systems
104	R-600a/142b/227ea/22	4/20/45/31	A-	14	Ex4 with less R-22, lower pressures, usable in some systems
105	R-600a/142b/227ea/22	4/8/32/56	C+	14	Ex4 with more R-22, higher pressures, usable in some systems
106	R-E170/142b/124/22	8/14.5/26.5/51	A+		Ex6 with more DME, weakly flammable, still usable
107	R-E170/142b/124/22	2/17.5/29.5/51	C		Ex6 with less DME, worse oil miscibility, still usable in some systems
108	R-E170/142b/124/22	4/21.5/23.5/41	A		Ex6 with less R-22, lower pressures, usable in some systems
109	R-E170/142b/124/22	4/9/21/66	B-		Ex6 with more R-22 higher pressures, usable in some systems
110	R-600a/142b/124/125	8/16/30/46	A	15	Ex58 with more isobutane, weakly flammable, still usable
111	R-600a/142b/124/125	2/19/33/48	C	15	Ex58 with less isobutane, worse oil misc., usable in some systems
112	R-600a/142b/124/125	4/23/37/36	A-	15	Ex58 with less R-125, lower pressures, usable in some systems
113	R-600a/142b/124/125	4/11/24/61	C-	15	Ex58 with more R-125, higher pressures, usable in some systems

There exist thousands of possible combinations and permutations from the refrigerant fluids listed in Tables 1-3 that could produce a refrigerant substitute for R-12. Many combinations can be ruled out under conditions 1,2, and 3 listed above. Other combinations may still provide a good 5 refrigerant, but may not be currently environmentally acceptable, but they may become acceptable in the future as new evidence and understanding of the environment proceeds. In general, higher temperature applications (above 32 degrees Fahrenheit and above such as automotive air conditioning) may work with R-12 substitutes that have poor or marginal oil 10 miscibility, whereas the same substitute may prove unacceptable in lower temperature applications such as freezers or refrigerators. Other combinations from Tables 1-3 may produce R-12 "drop-in" substitutes that have low critical temperatures, below about 215 degrees Fahrenheit, and still provide satisfactory performance in the majority of climates, but prove 15 unsatisfactory in extreme heat or very high humidity climates.

For any given combination of components, from Tables 1-3, above, that produce a useable "drop-in" substitute for R-12, many permutations (ranges) of each component's weight percentage are possible. Work to date has shown that highly flammable GROUP-B oil miscibility improvers 20 (isobutane, dimethyl ether, propane, etc) still provide some oil miscibility improvement in concentrations as low as about 1 weight percent (see discussion in Condition 2, above). Highly flammable GROUP-B components may be further increased to about 10 weight percent if a weakly flammable refrigerant can be tolerated, giving a range of about 1 to 10 weight percent in 25 most cases for a useable "drop-in" substitute for R-12. GROUP-C components (see discussion in Condition 1, above), may be varied over the range of about -10 to +15 weight percent from their "normal centerline" values

-50-

used to create a normal temperature-pressure curve. This allows for special uses such as "low capacity" and "high capacity" refrigerant mixtures.

Adjustment of weight percentages of GROUP-C components, must be accompanied by a corresponding opposite adjustment in GROUP-A

5 components so that the total of all weight percentages remains at 100 percent. Examples 98-113 in Table 6, above, illustrate component ranges applied to Examples 1, 4, and 6, also in Table 6.

Appendix A

The oil miscibility test stand consists of:

10 A refrigeration test stand built from a new two-ton medium temperature R-12 semi-hermetic Copeland compressor, model EAL2-0200-CAB. A standard two ton condenser (R-22) and fan were salvaged from a residential central air conditioning system. The oil test stand is a standard refrigeration system consisting of a compressor, a condenser, a refrigerant metering device (manual expansion valve) and an evaporator. The object of said test stand is to try to force oil logging (poor oil return) to occur in order to evaluate the oil return capabilities of test refrigerant mixtures under worst case conditions.

15 The evaporator is a 50 foot coil of 5/8" refrigeration copper tubing, in free air, with no fan or fins. The coil diameter is around 14 inches and is

20 spread out to be about 2 1/2 feet deep. The centerline of the coil is parallel to the ground, providing each loop (11 of them) a chance to "trap" oil. There are six refrigeration sight glasses, or viewing ports in the refrigeration circuit. They are located, in the liquid line, just before the refrigerant metering (expansion) needle valve, just after the metering valve, midway in the 25 evaporator, at the bottom of the center turn of pipe, at the evaporator outlet, in the center of the 6 foot vertical riser 7/8" suction line, and in the center of the 6 foot horizontal suction line run.

-51-

Evaporator heat can be provided from direct electric heating of the coil, up to 310 Amps, approximately 5 volts from a variable DC power supply. The liquid line has a 1 foot rubber hose (automotive barrier hose) segment to block current flow through the condenser and compressor.

5 The (hand operated) metering device is a multiturn needle valve, approximately 4 tons capacity wide open.

The suction line, is a 6 foot piece of 7/8" vertical (straight up) copper, followed, by a 6 foot horizontal run (also 7/8"). The horizontal run has a "low spot", about 1 inch lower than the ends, for oil to collect in (and a sight glass).

10 There is also a manual EPR (evaporator pressure regulator - ball valve, with 3/4" opening), with low side gauges on either side of the valve.

What is claimed is:

1. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 7 to 34 weight percent 1-chloro-1,1-difluoroethane, about 5 to 50 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, and about 35 to 75 weight percent chlorodifluoromethane, with the weight percentages of said components being weight percentages of the overall mixture.

2. The mixture of refrigerants of claim 1 in which isobutane is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 13 to 16.5 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 28.5 to 33 weight percent, and chlorodifluoromethane is present in about 50 to 51 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

3. The mixture of refrigerants of claim 1 in which isobutane is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 34 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 7 weight percent, and chlorodifluoromethane is present in about 55 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

4. The mixture of refrigerants of claim 1 in which isobutane is present in about 1.5 weight percent, 1-chloro-1,1-difluoroethane is present in

about 9.5 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 39 weight percent, and chlorodifluoromethane is present in about 50 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

5 5. The mixture of refrigerants of claim 1 in which isobutane is present in about 3 to 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 14.5 to 18 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 20.5 to 24 weight percent, and chlorodifluoromethane is present in about 55 to 61 weight percent, the weight percentages of said 10 components being weight percentages of the overall mixture.

6. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigerant systems, comprising about 1 to 10 weight percent isobutane, about 5 to 25 weight percent 1-chloro-1,1-difluoroethane, about 15 to 60 weight percent 15 heptafluoropropane, and about 21 to 75 weight percent chlorodifluoromethane, with the weight percentages of said components being weight percentages of the overall mixture.

7. The mixture of refrigerants of claim 6 in which isobutane is present in about 4 weight percent isobutane, 1-chloro-1,1-difluoroethane is present in about 15 weight percent, heptafluoropropane is present in about 40 weight percent, and chlorodifluoromethane is present in about 41 weight percent, the weight percentages of said components being weight 20 percentages of the overall mixture.

8. The mixture of refrigerants of claim 6 in which isobutane is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 15 weight percent, heptafluoropropane is present in about 30 weight percent, and chlorodifluoromethane is present in about 51 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

5

9. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigerant systems, comprising about 1 to 10 weight percent isobutane, about 8 to 30 weight percent 1-chloro-1,1-difluoroethane, about 9 to 50 weight percent 10 2-chloro-1,1,1,2-tetrafluoroethane, about 28 to 70 weight percent chlorodifluoromethane, and about 1 to 20 weight percent of a refrigerant selected from the group consisting of heptafluoropropane, propane, propylene, and dimethyl ether, with the weight percentages of said 15 components being weight percentages of the overall mixture.

10

10. The mixture of refrigerants in claim 9 in which isobutane is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 15 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 17 weight percent, chlorodifluoromethane is present in about 44 weight percent, and heptafluoropropane is present in about 20 weight percent, the weight percentages of said components being weight percentages of the 20 overall mixture.

20

11. The mixture of refrigerants of claim 9 in which isobutane is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in

about 16 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 22 to 32 weight percent, chlorodifluoromethane is present in about 44 to 54 weight percent, and propane is present in about 4 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

5

12. The mixture of refrigerants in claim 9 in which isobutane is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 16 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 33 weight percent, chlorodifluoromethane is present in about 43 weight percent, and propylene is present in about 4 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

10

13. The mixture of refrigerants of claim 9 in which isobutane is present in about 2 weight percent, 1-chloro-1,1-difluoroethane is present in about 17 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 29 weight percent, chlorodifluoromethane is present in about 50 weight percent, and dimethyl ether is present in about 2 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

15

20 14. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent dimethyl ether, about 5 to 35 weight percent 1-chloro-1,1-difluoroethane, about 10 to 40 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, about 30 to 70 weight percent

chlorodifluoromethane, and about 0 to 10 weight percent of a refrigerant selected from the group consisting of propane and methyl trifluoromethyl ether with the weight percentages of said components being weight percentages of the overall mixture.

5 15. The mixture of refrigerants of claim 14 in which dimethyl ether is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 14.5 to 16.5 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 20.5 to 28.5 weight percent, and chlorodifluoromethane is present in about 51 to 61 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

10 16. The mixture of refrigerants of claim 14 in which dimethyl ether is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 17 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 29 weight percent, chlorodifluoromethane is present in about 46 weight percent, and propane is present in about 4 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

15 17. The mixture of refrigerants of claim 14 in which dimethyl ether is present in about 5 weight percent, 1-chloro-1,1-difluoroethane is present in about 12 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 28 weight percent, chlorodifluoromethane is present in about 50 weight percent, and methyl trifluoromethyl ether is present in about 5 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

18. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 28 to 58 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, about 5 to 30 weight percent 5 1,1,1,2-tetrafluoroethane, about 4 to 28 weight percent 1,1,1-trifluoroethane, about 4 to 28 weight percent pentafluoroethane, and about 1 to 20 weight percent hexafluoropropene, with the weight percentages of said components being weight percentages of the overall mixture.

19. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 5 to 30 weight percent 10 1-chloro-1,1-difluoroethane, about 5 to 30 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, about 10 to 45 weight percent 1,1,1,2-tetrafluoroethane, about 1 to 10 weight percent propane, and about 15 20 to 60 weight percent chlorodifluoromethane, with the weight percentages of said components being weight percentages of the overall mixture.

20. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent propane, about 20 to 60 weight percent 20 1-chloro-1,1-difluoroethane, about 30 to 74 weight percent chlorodifluoromethane, and about 0 to 10 weight percent isobutane, with the weight percentages of said components being weight percentages of the overall mixture.

21. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 5 to 30 weight percent 1-chloro-1,1-difluoroethane, about 15 to 50 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, about 30 to 60 weight difluoromethyltrifluoromethyl ether, and about 0 to 10 weight percent of a refrigerant selected from the group consisting of propane and propylene, with the weight percentages of said components being weight percentages of the overall mixture.

10 22. The mixture of refrigerants of claim 21 in which isobutane is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 16 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 33 weight percent, difluoromethyltrifluoromethyl ether is present in about 43 weight percent, and propane is present in about 4 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

15 23. The mixture of refrigerants of claim 21 in which isobutane is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 16 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 32 weight percent, difluoromethyltrifluoromethyl ether is present in about 44 weight percent, and propylene is present in about 4 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

24. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising 1 to 10 weight percent isobutane, about 32 to 65 weight percent 1-chloro-1,1-difluoroethane, 5 about 29 to 65 weight percent pentafluoroethane, and about 0 to 10 weight percent of a refrigerant selected from the group consisting of propane and propylene with the weight percentages of said components being weight percentages of the overall mixture.

25. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 6 to 31 weight percent 1-chloro-1,1-difluoroethane, about 20 to 65 weight percent heptafluoropropane, and about 22 to 58 weight percent pentafluoroethane, 10 with the weight percentages of said components being weight percentages of the overall mixture, 15

26. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 31 to 60 weight percent 1-chloro-1,1-difluoroethane, about 15 to 40 weight percent 20 chlorodifluoromethane, about 13 to 38 weight percent pentafluoroethane, and about 1 to 10 weight percent of a refrigerant selected from the group consisting of propane and propylene with the weight percentages of said components being weight percentages of the overall mixture.

27. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 15 to 58 weight percent 1-chloro-1,1-difluoroethane, about 4 to 20 weight percent 5 1,1,1,2-tetrafluoroethane, about 30 to 60 weight percent chlorodifluoromethane, and about 1 to 10 weight percent of a refrigerant selected from the group consisting of propane and propylene, with the weight percentages of said components being weight percentages of the overall mixture.

10 28. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 30 to 65 weight percent 15 2-chloro-1,1,1,2-tetrafluoroethane, about 28 to 67 weight percent chlorodifluoromethane, and about 0 to 10 weight percent of a refrigerant selected from the group consisting of propane and propylene, with the weight percentages of said components being weight percentages of the overall mixture.

20 29. The mixture of refrigerants of claim 28 in which isobutane is present in about 4 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 52 weight percent, chlorodifluoromethane is present in about 40 weight percent, and propane is present in about 4 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

30. The mixture of refrigerants of claim 28 in which isobutane is present in about 4 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 53 weight percent, chlorodifluoromethane is present in about 39 weight percent, and propylene is present in about 4 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

5

31. The mixture of refrigerants of claim 28 in which isobutane is present in about 6 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 48 weight percent, chlorodifluoromethane is present in about 42 weight percent, and propane is present in about 4 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

10

32. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 41 to 85 weight percent heptafluoropropane, about 8 to 40 weight percent chlorodifluoromethane, about 1 to 10 weight percent propane, and about 0 to 25 weight percent 1,1,1,2-tetrafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

15

20

33. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 50 to 78 weight percent 1,1,1,2,2-pentafluoropropane, about 15 to 55 weight percent chlorodifluoromethane, and about 1 to 10 weight percent propane, with the

-62-

weight percentages of said components being weight percentages of the overall mixture.

34. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent dimethyl ether, about 25 to 50 weight percent 1-chloro-1,1-difluoroethane, about 30 to 76 weight percent chlorodifluoromethane, and about 1 to 10 weight percent of a refrigerant from the group consisting of isobutane and propane.

35. The mixture of refrigerants of claim 34 in which dimethyl ether is present in about 2 weight percent, isobutane is present in about 2 weight percent, 1-chloro-1,1-difluoroethane is present in about 41 weight percent, and chlorodifluoromethane is present in about 55 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

36. The mixture of refrigerants of claim 34 in which dimethyl ether is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 41 weight percent, chlorodifluoromethane is present in about 61 weight percent, and propane is present in about 4 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

37. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent dimethyl ether, about 34 to

76 weight percent heptafluoropropane, about 10 to 35 weight percent pentafluoroethane, about 1 to 10 weight percent propane, and about 5 to 30 weight percent of a refrigerant selected from the group consisting of 1,1,1-trifluoroethane and 1,1,1,2-tetrafluoroethane, with the weight 5 percentages of said mixture being weight percentages of the overall mixture.

38. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerants in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent dimethyl ether, about 55 to 85 weight percent heptafluoropropane, about 9 to 37 weight percent 10 pentafluoroethane, and about 1 to 10 weight percent propane, with the weight percentages of said components being weight percentages of the overall mixture.

39. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration 15 systems, comprising about 1 to 10 weight percent isobutane, about 32 to 76 weight percent heptafluoropropane, about 10 to 32 weight percent 1,1,1,2-tetrafluoroethane, about 1 to 10 weight percent propane, and about 9 to 31 weight percent of a refrigerant selected from the group consisting of 20 1,1,1-trifluoroethane and pentafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

40. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 28 to 63 weight percent 1-chloro-1,1-difluoroethane, about 37 to 71 weight percent

difluoromethyltrifluoromethyl ether, and about 0 to 8 weight percent propane, with the weight percentages of said components being weight percentages of said overall mixture.

41. A mixture of refrigerants that is a drop-in substitute for
5 dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 8 to 35 weight percent 1-chloro-1,1-difluoroethane, about 12 to 51 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, about 29 to 63 weight percent pentafluoroethane and about 0 to 10 weight percent propane, with the weight
10 percentages of said components being weight percentages of the overall mixture.

42. The mixture of refrigerants of claim 41 in which isobutane is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 18 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in
15 about 32 weight percent, and pentafluoroethane is present in about 46 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

43. The mixture of refrigerants of claim 41 in which isobutane is present in about 4 weight percent, 1-chloro-1,1-difluoroethane is present in about 18 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in
20 about 32 weight percent, pentafluoroethane is present in about 42 weight percent, and propane is present in about 4 weight percent, the weight percentages of said components being the weight percentages of the overall mixture.

44. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 5 to 32 weight percent 1-chloro-1,1-difluoroethane, about 8 to 45 weight percent 5 heptafluoropropane, about 6 to 35 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, and about 25 to 60 weight percent pentafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

45. A mixture of refrigerants that is a drop-in substitute for 10 dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 30 to 74 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, about 22 to 66 weight percent pentafluoroethane, and about 0 to 10 weight percent of a refrigerant 15 selected from the group consisting of propane and propylene, with the weight percentages of said components being weight percentages of said overall mixture.

46. The mixture of refrigerants of claim 45 in which isobutane is 20 present in about 8 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 51 weight percent, and pentafluoroethane is present in about 41 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

47. The mixture of refrigerants of claim 45 in which isobutane is 25 present in about 6 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is

present in about 54 weight percent, pentafluoroethane is present in about 36 weight percent, and propane is present in about 4 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

5 48. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in a dichlorodifluoromethane refrigeration system, comprising about 1 to 10 weight percent dimethyl ether, about 35 to 72 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, about 24 to 60 weight percent pentafluoroethane, and about 0 to 10 weight percent of a refrigerant
10 selected from the group consisting of propane and propylene, with the weight percentages of said components being weight percentages of the overall mixture.

15 49. The mixture of refrigerants of claim 48 in which dimethyl ether is present in about 8 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 51 weight percent, and pentafluoroethane is present in about 41 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

20 50. The mixture of refrigerants of claim 48 in which dimethyl ether is present in about 6 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 54 weight percent, pentafluoroethane is present in about 36 weight percent, and propane is present in about 4 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

51. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 12 weight percent dimethyl ether, about 31 to 67 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, about 28 to 65 weight percent chlorodifluoromethane, and about 0 to 10 weight percent of a refrigerant selected from the group consisting of propane and propylene, with the weight percentages of said components being weight percentages of the overall composition.

52. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 58 to 85 weight percent heptafluoropropane, about 9 to 35 weight percent pentafluoroethane, and about 1 to 10 weight percent of a refrigerant selected from the group consisting of propane and propylene with the weight percentages of said components being weight percentages of the overall mixture.

53. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 2 to 12 weight percent isobutane, about 19 to 48 weight percent heptafluoropropane, about 18 to 42 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, and about 20 to 55 weight percent pentafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

54. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent dimethyl ether, about 33 to 72 weight percent 1-chloro-1,1-difluoroethane, about 30 to 65 weight percent 5 pentafluoroethane, and about 1 to 10 weight percent of a refrigerant selected from the group consisting of propane and propylene, with the weight percentages of said components being weight percentages of the overall mixture.

10 55. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 31 to 68 weight percent 1-chloro-1,1-difluoroethane, about 25 to 62 weight percent pentafluoroethane, about 1 to 10 weight percent propane and about 0 to 20 weight percent 15 1,1,1,2-tetrafluoroethane, with the weight percentages of said components being the weight percentages of the overall mixture.

20 56. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent dimethyl ether, about 58 to 85 weight percent heptafluoropropane, about 8 to 35 weight percent pentafluoroethane, and about 1 to 10 weight percent propylene, with the weight percentages of said components being weight percentages of the overall mixture.

57. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration

systems, comprising about 31 to 71 weight percent 1-chloro-1,1-difluoroethane, about 23 to 61 weight percent pentafluoroethane, about 1 to 10 weight percent propylene, and about 0 to 20 weight percent 1,1,1,2-tetrafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

5 58. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 15 to 59 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, about 10 to 59 weight percent 1,1,1,2-tetrafluoroethane, and about 15 to 54 weight percent of a refrigerant selected from the group consisting of chlorodifluoromethane, pentafluoroethane, and 1,1,1-trifluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

10 59. The mixture of refrigerants of claim 58 in which isobutane is present in about 6 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 26 weight percent, 1,1,1,2-tetrafluoroethane is present in about 40 weight percent, and chlorodifluoromethane is present in about 28 weight percent, the weight percentages of said components being weight percentages of the overall mixture.

15 60. The mixture of refrigerants of claim 58 in which isobutane is present in about 6 weight percent, 2-chloro-1,1,1,2-tetrafluoroethane is present in about 37 weight percent, 1,1,1,2-tetrafluoroethane is present in about 26 weight percent, and chlorodifluoromethane is present in about 28

weight percent, the weight percentages of said components being weight percentages of the overall mixture.

61. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 60 to 92 weight percent heptafluoropropane and about 8 to 40 weight percent chlorodifluoromethane, with the weight percentages of said components being weight percentages of the overall mixture.

62. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 27 to 67 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, about 1-chloro-1,1-difluoroethane, and about 18 to 58 weight percent pentafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

63. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 4 to 16 weight percent 1-chloro-1,1-difluoroethane, about 5 to 20 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, and about 60 to 90 weight percent perfluoropropane, with the weight percentages of said components being weight percentages of the overall mixture.

64. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 28 to 65 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, about 15 to 48 weight percent 1,1,1,2-tetrafluoroethane, and about 1 to 25 weight percent of a refrigerant selected from the group consisting of propane and pentafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

5 65. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 8 weight percent isobutane, about 24 to 61 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, about 14 to 40 weight percent 1,1,1,2-tetrafluoroethane, about 1 to 8 weight percent propane, and about 14 to 43 weight percent of a refrigerant selected from the group 10 consisting of pentafluoroethane and chlorodifluoromethane, with the weight percentages of said components being weight percentages of the overall mixture.

15 66. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 28 to 60 weight percent heptafluoropropane, about 8 to 33 weight percent 1-chloro-1,1-difluoroethane, and about 25 to 60 weight percent chlorodifluoromethane, with the weight percentages of said components being weight percentages of the overall mixture.

67. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent dimethyl ether, about 55 to 89 weight percent heptafluoropropane, and about 8 to 43 weight percent of a refrigerant selected from the group consisting of chlorodifluoromethane, pentafluoroethane, and 1,1,1-trifluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

68. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 15 to 48 weight percent 1-(trifluoromethoxy)-1,1,2,2-tetrafluoroethane, about 1 to 10 weight percent isobutane, about 52 to 80 weight percent perfluoropropane, and about 1 to 10 weight percent of a refrigerant selected from the group consisting of propane and propylene, with the weight percentages of said components being weight percentages of the overall mixture.

69. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 18 to 40 weight percent octafluorocyclobutane, about 1 to 10 weight percent dimethyl ether, about 51 to 86 weight percent perfluoropropane, and about 1 to 10 weight percent propane, with the weight percentages of said components being weight percentages of the overall mixture.

70. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 1 to 10 weight percent isobutane, about 55 to 85

weight percent heptafluoropropane, and about 13 to 43 weight percent of a refrigerant selected from the group consisting of pentafluoroethane and 1,1,1,-trifluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

5 71. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 28 to 70 weight percent 1-chloro-1,1-difluoroethane and about 30 to 72 weight percent pentafluoroethane, with the weight percentages of said components being
10 weight percentages of the overall mixture.

72. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 37 to 77 weight percent 1-chloro-1,1-difluoroethane and about 23 to 63 weight percent
15 1,1,1-trifluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

73. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 48 to 88 weight percent
20 2-chloro-1,1,1,2-tetrafluoroethane and about 12 to 52 weight percent 1,1,1-trifluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

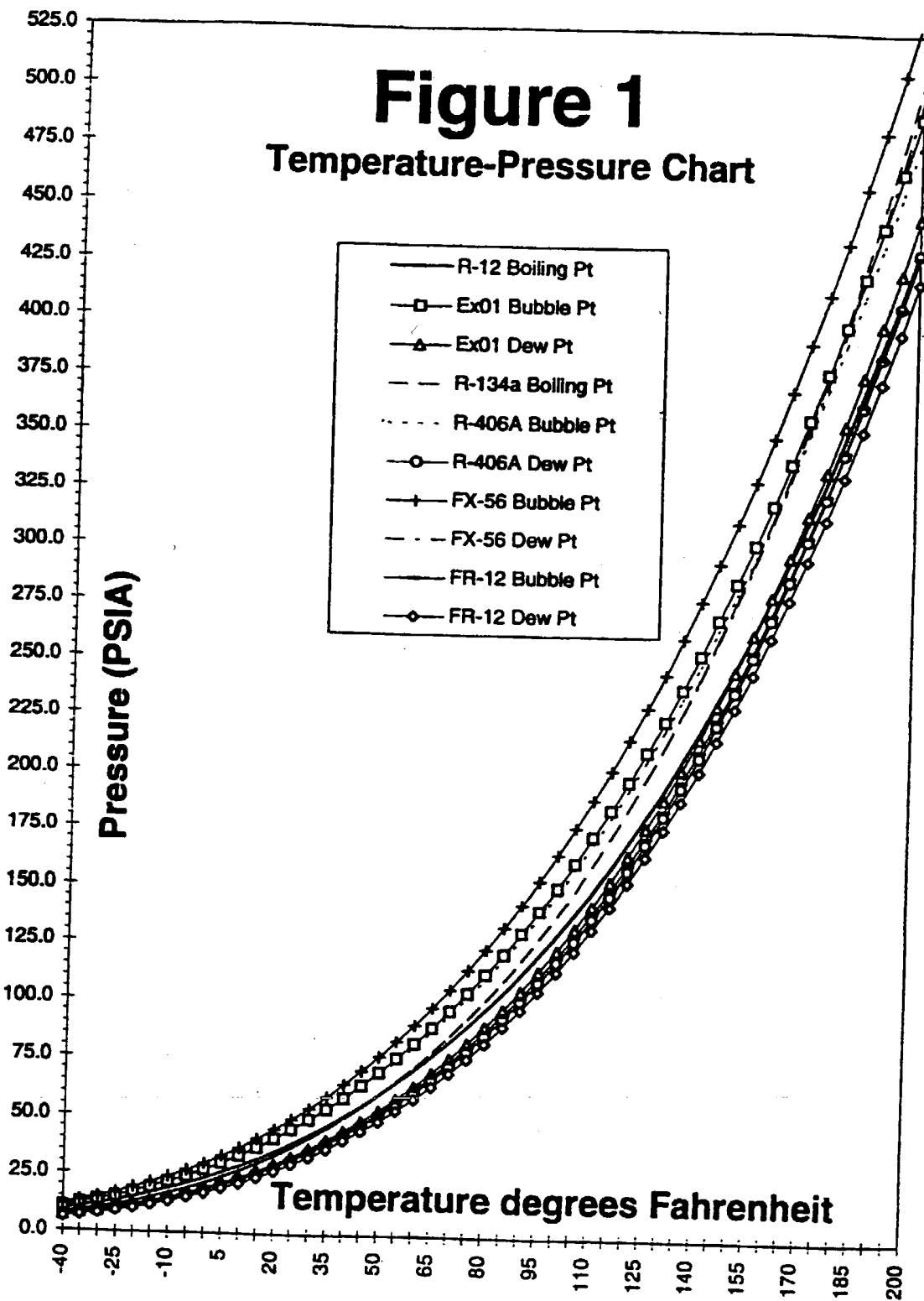
74. A mixture of refrigerants that is a drop-in substitute for dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising about 0.5 to 8 weight percent isobutane, about 15 to 60 weight percent of a component B, and about 21 to 71 weight percent 5 chlorodifluoromethane, with the weight percentages of the foregoing components being weight percentages of the overall mixture, wherein component B is about 99 weight percent 1-chloro-1,1-difluoroethane and about 1 to 99 weight percent of a component C, with the weight percentages of the subcomponents of component B being weight percentages of 10 component B, wherein component C is about 0 to 100 weight percent heptafluoropropane and about 0 to 100 weight percent 2-chloro-1,1,1,2-tetrafluoroethane, with the weight percentages of the components of component C being weight percentages of component C.

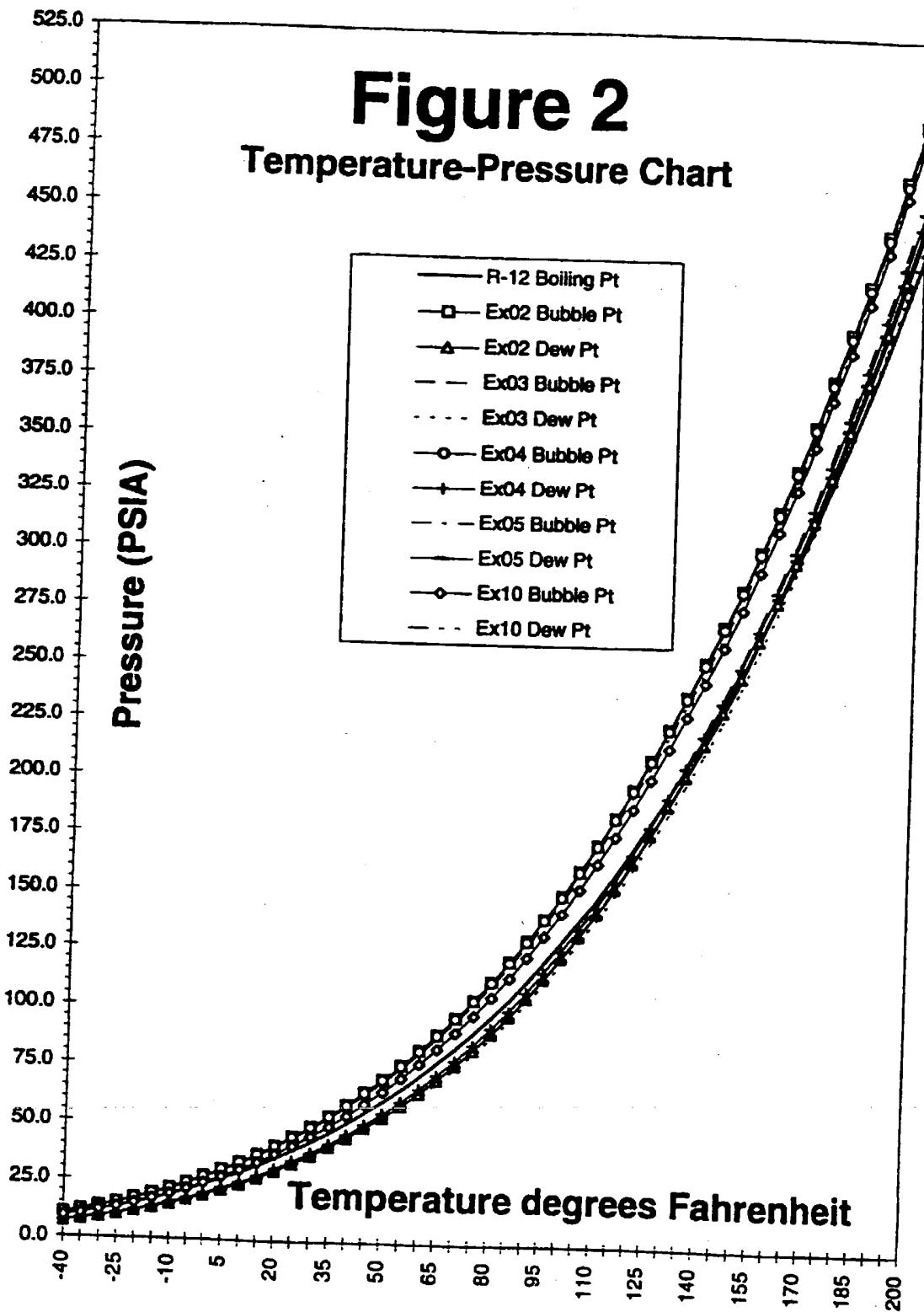
75. A mixture of refrigerants that is a drop-in substitute for 15 dichlorodifluoromethane refrigerant in dichlorodifluoromethane refrigeration systems, comprising one or more components from GROUP A of Table 4, zero or more components from GROUP B of Table 4, one or more 20 components from GROUP C of Table 4, and zero or more components from GROUP D of Table 4, wherein the temperature versus pressure curve of a closed container of said mixture approximates, within about 15 to 30 percent error, the temperature versus pressure curve from about -40 °F to about 200 °F of a closed container of dichlorodifluoromethane refrigerant, and wherein 25 said mixture is sufficiently miscible with the mineral oils within dichlorodifluoromethane refrigeration systems so as to provide adequate circulating of the oils throughout the systems, and wherein the maximum mass fraction of said components that are very flammable is about 5 to 10

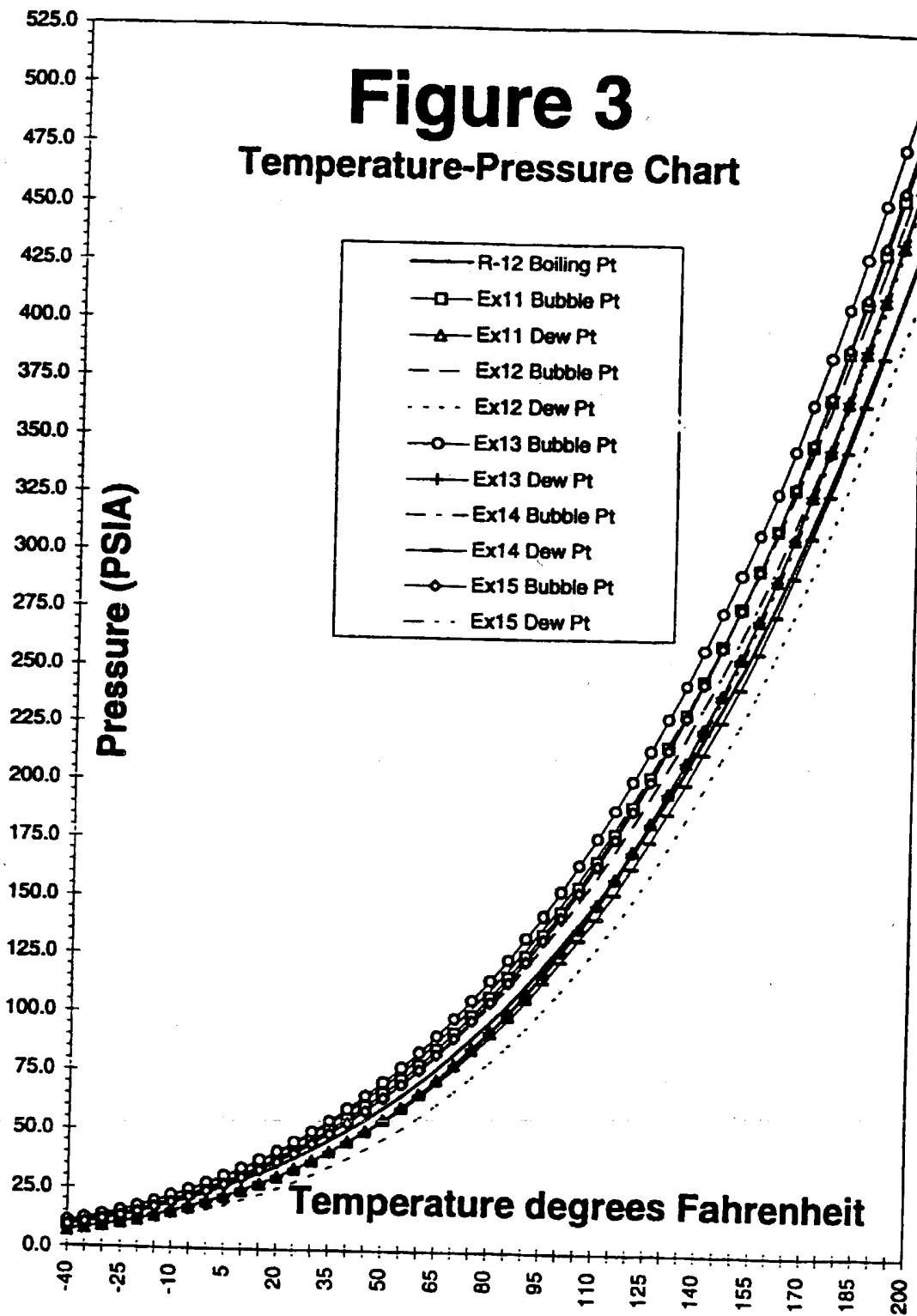
percent and the maximum mass fraction of said components that are weakly flammable is about 15 to about 60 percent, and wherein any halocarbon component that is mixed with two hydrocarbon components, one having a higher and one having a lower boiling point than said halocarbon component,

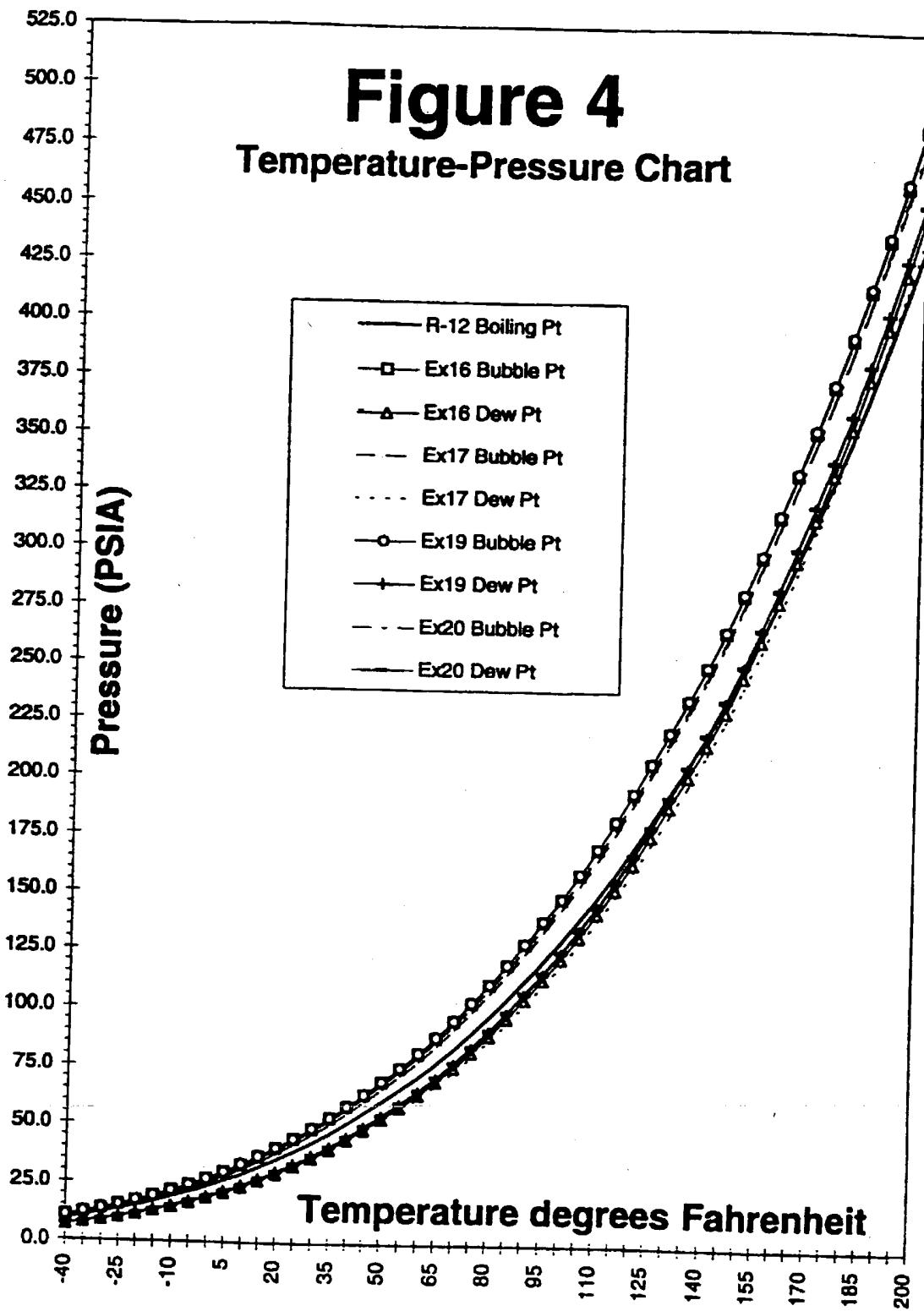
5 is at least a weakly flammable halocarbon, and wherein of any two halocarbon components that are mixed with a hydrocarbon component, that has a boiling point that is between the boiling points of said two halocarbon components, one of said halocarbon components is at least weakly flammable halocarbon; said mixtures of refrigerants being mixtures other than

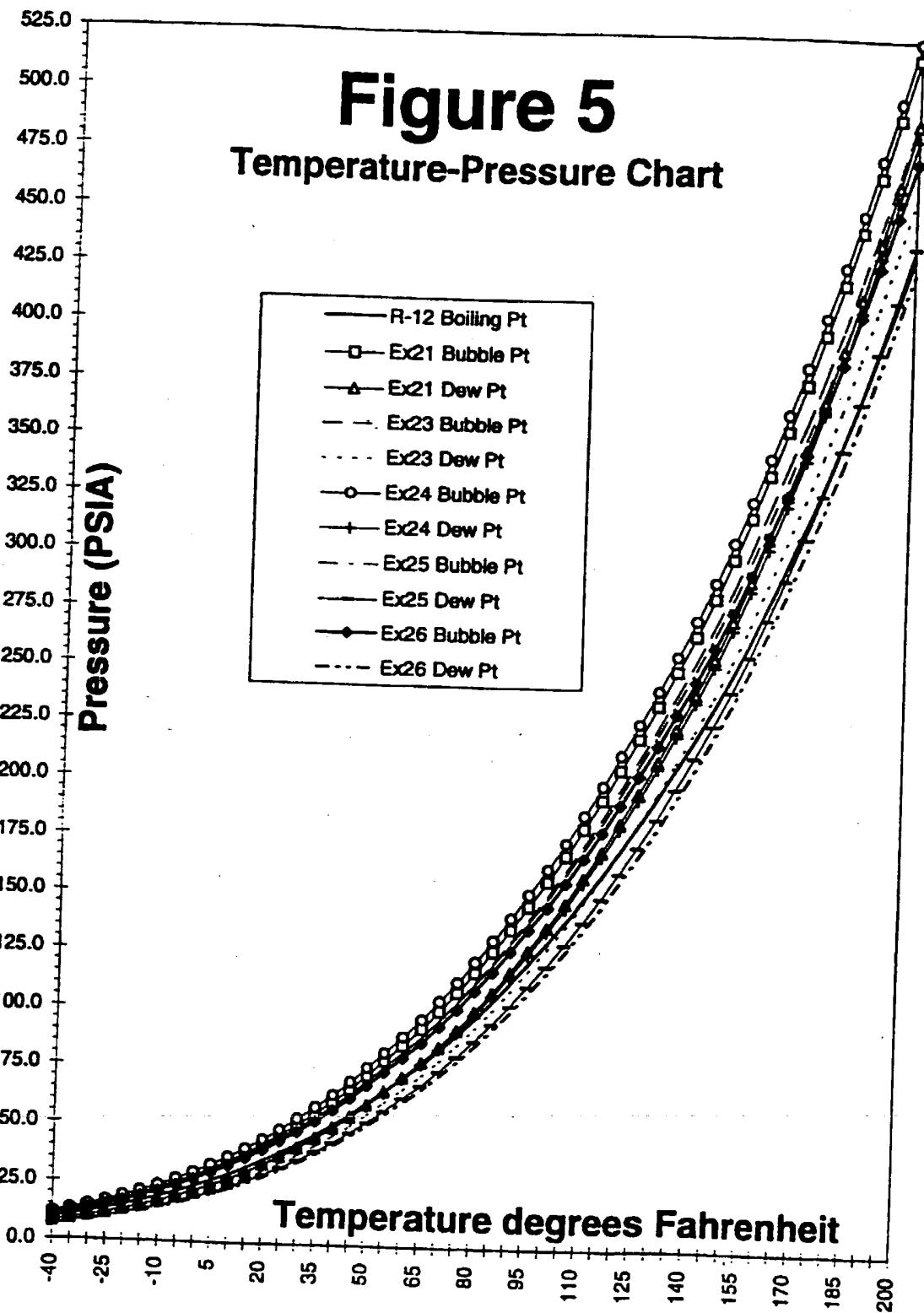
10 those comprising about 2 to 20 weight percent isobutane, about 21 to 51 weight percent 1-chloro-1,1-difluoroethane, and about 41 to 71 weight percent chlorodifluoromethane, wherein the weight percentages are weight percentages of the overall mixtures.

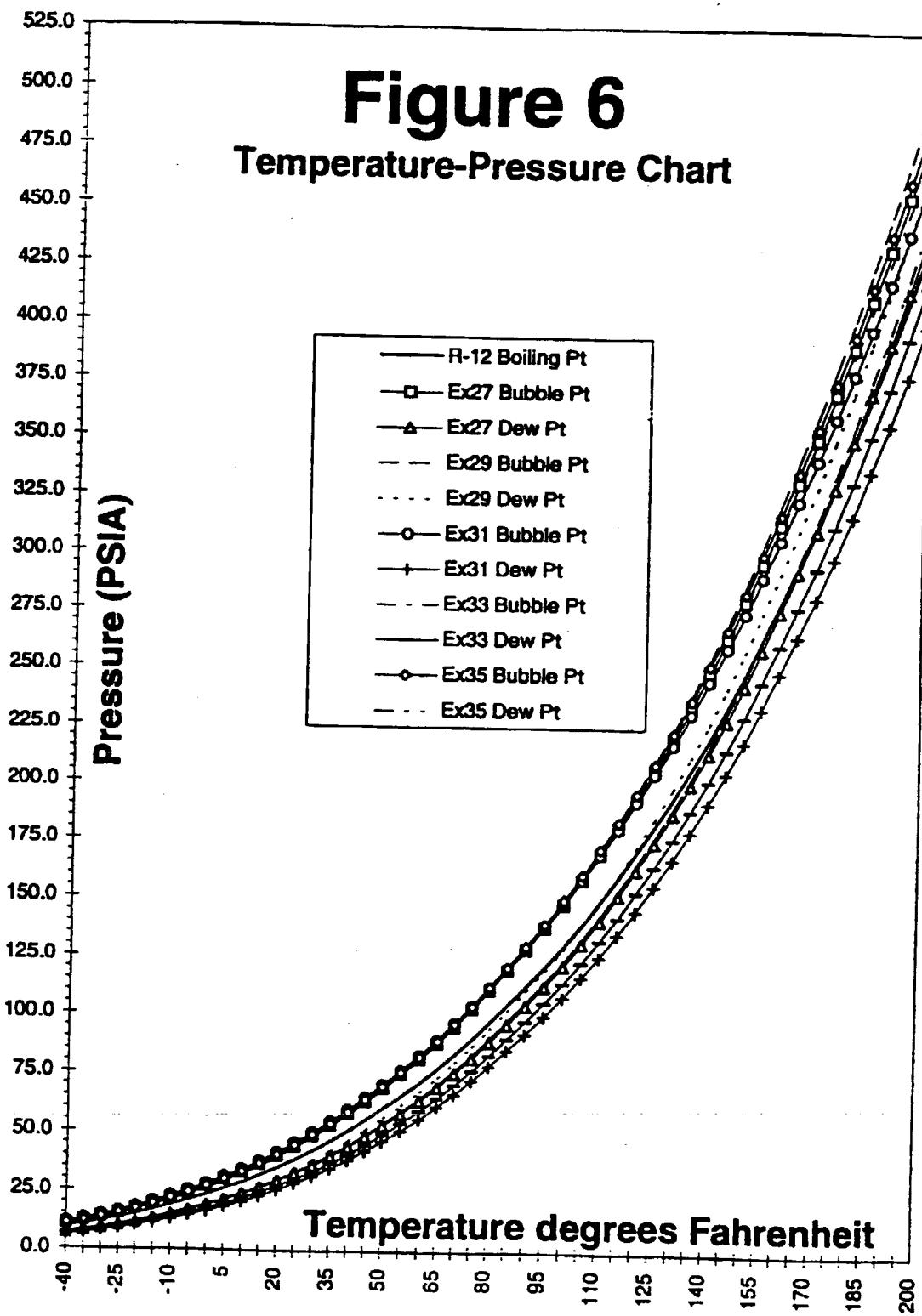


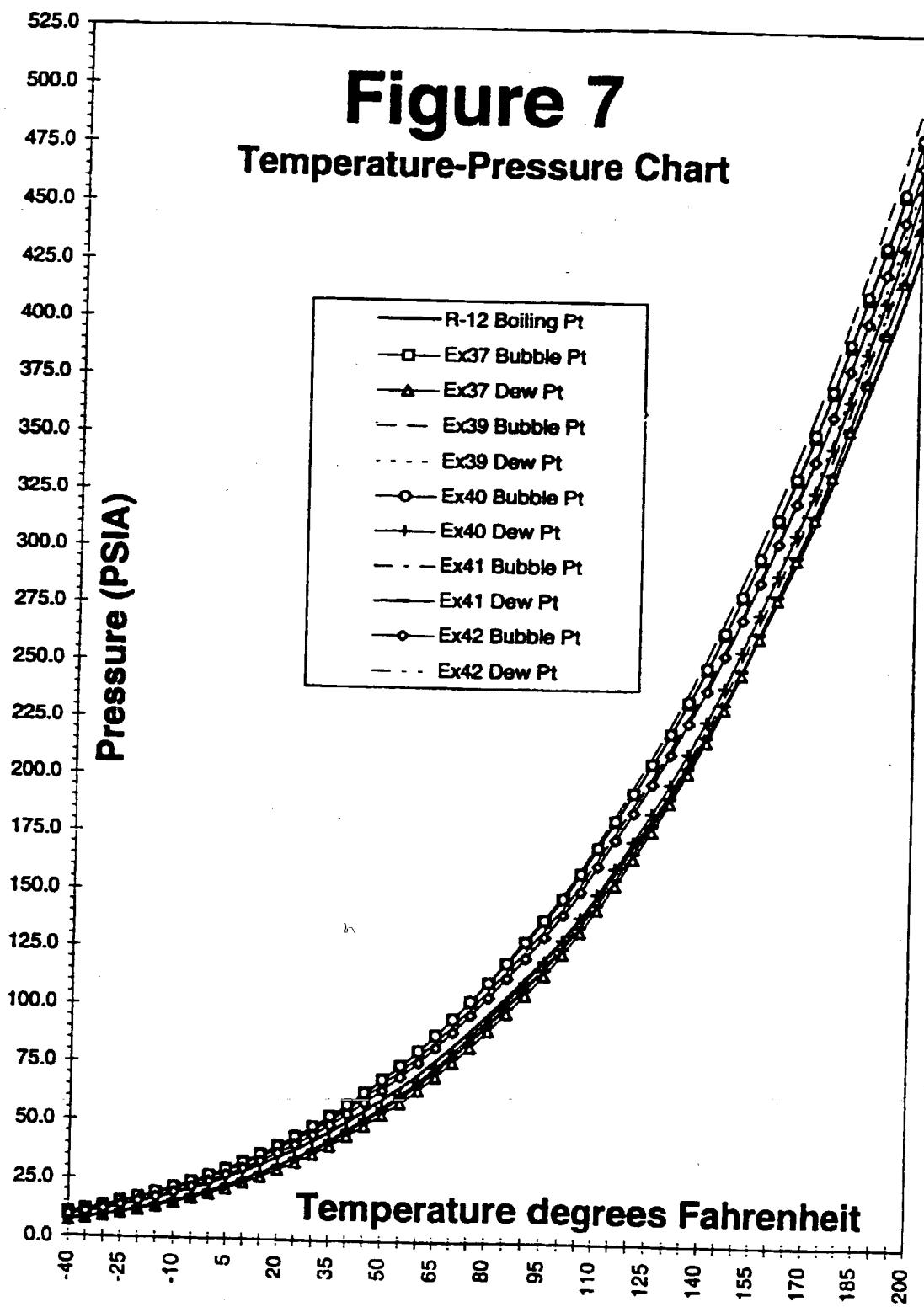


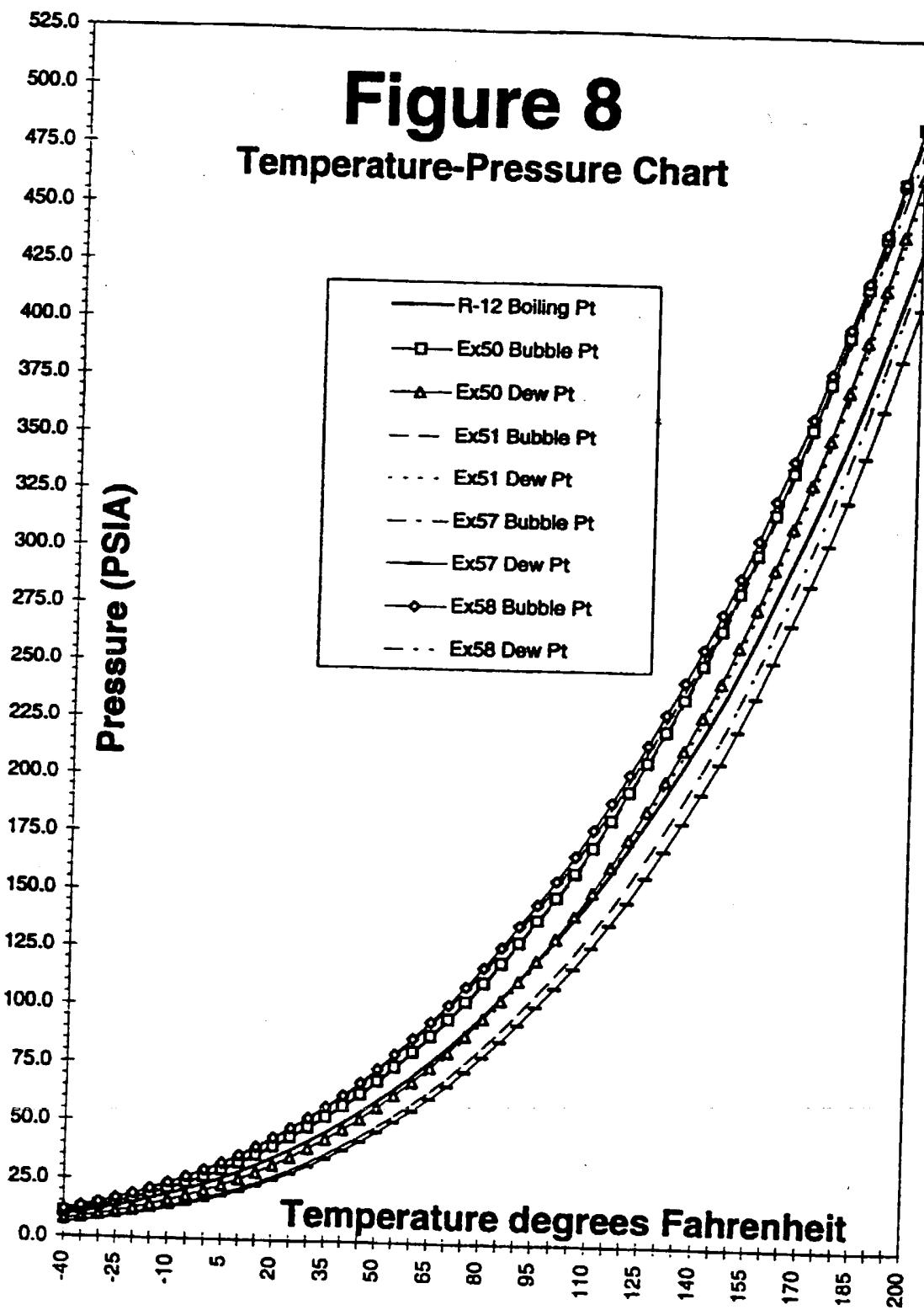


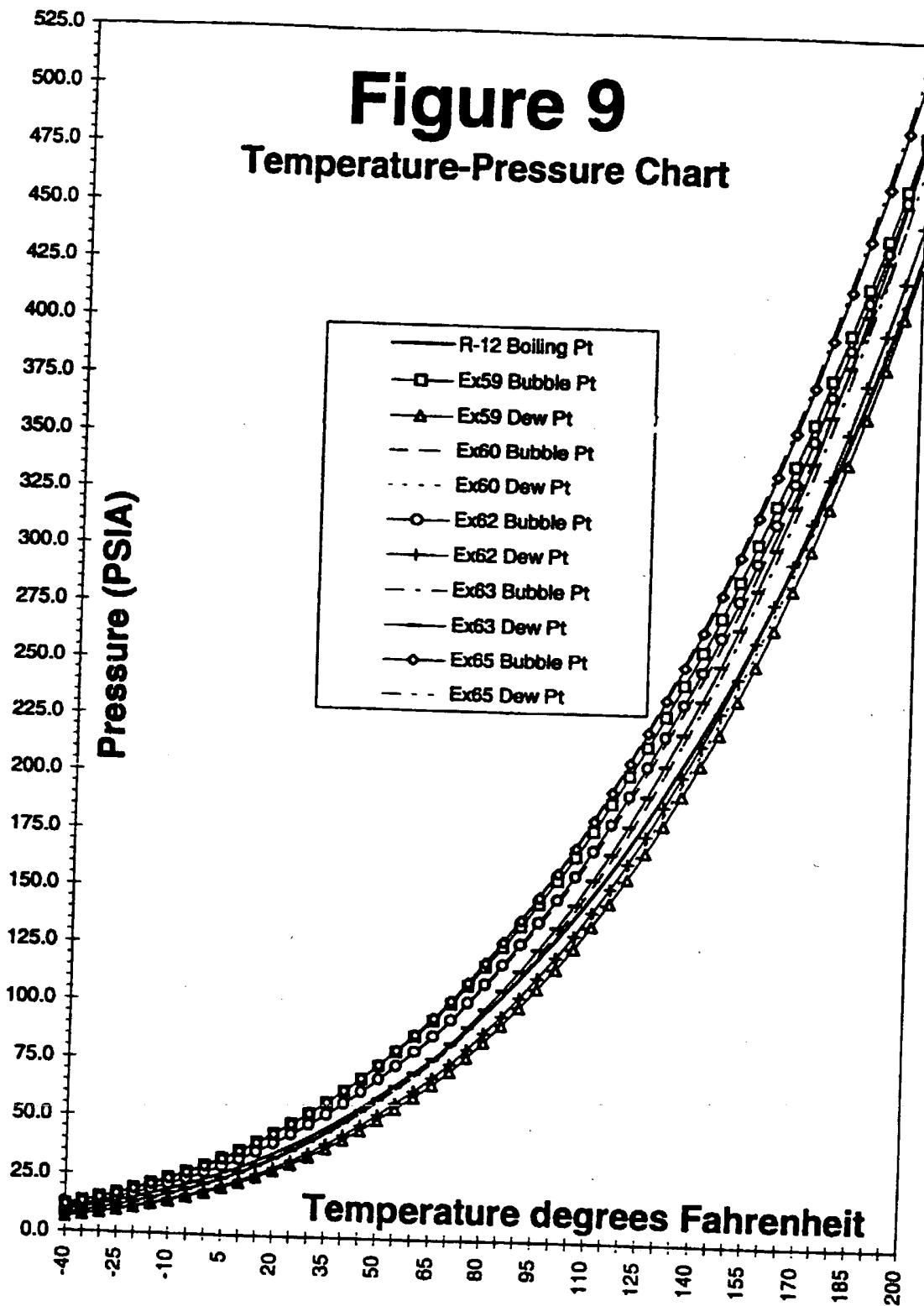


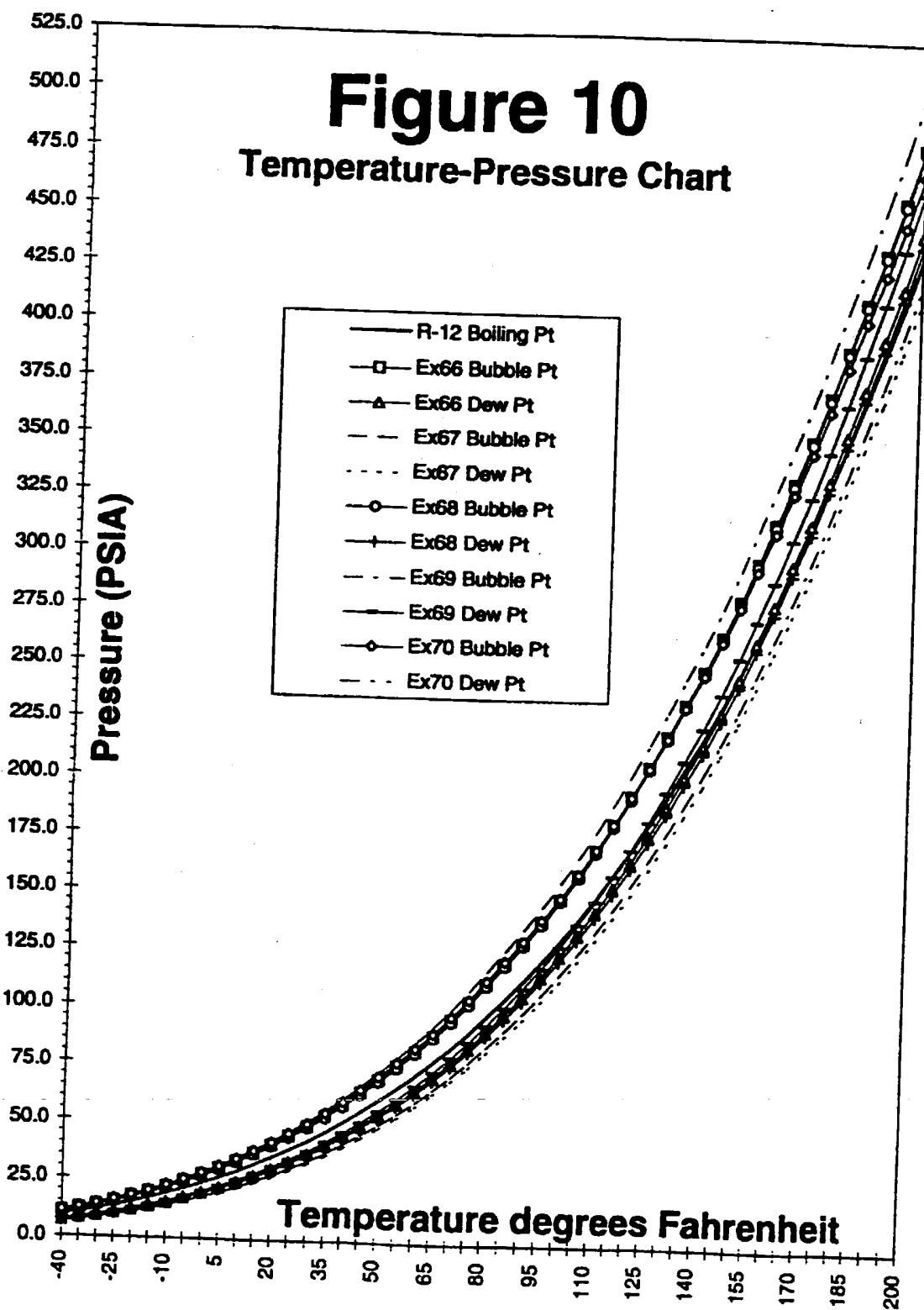


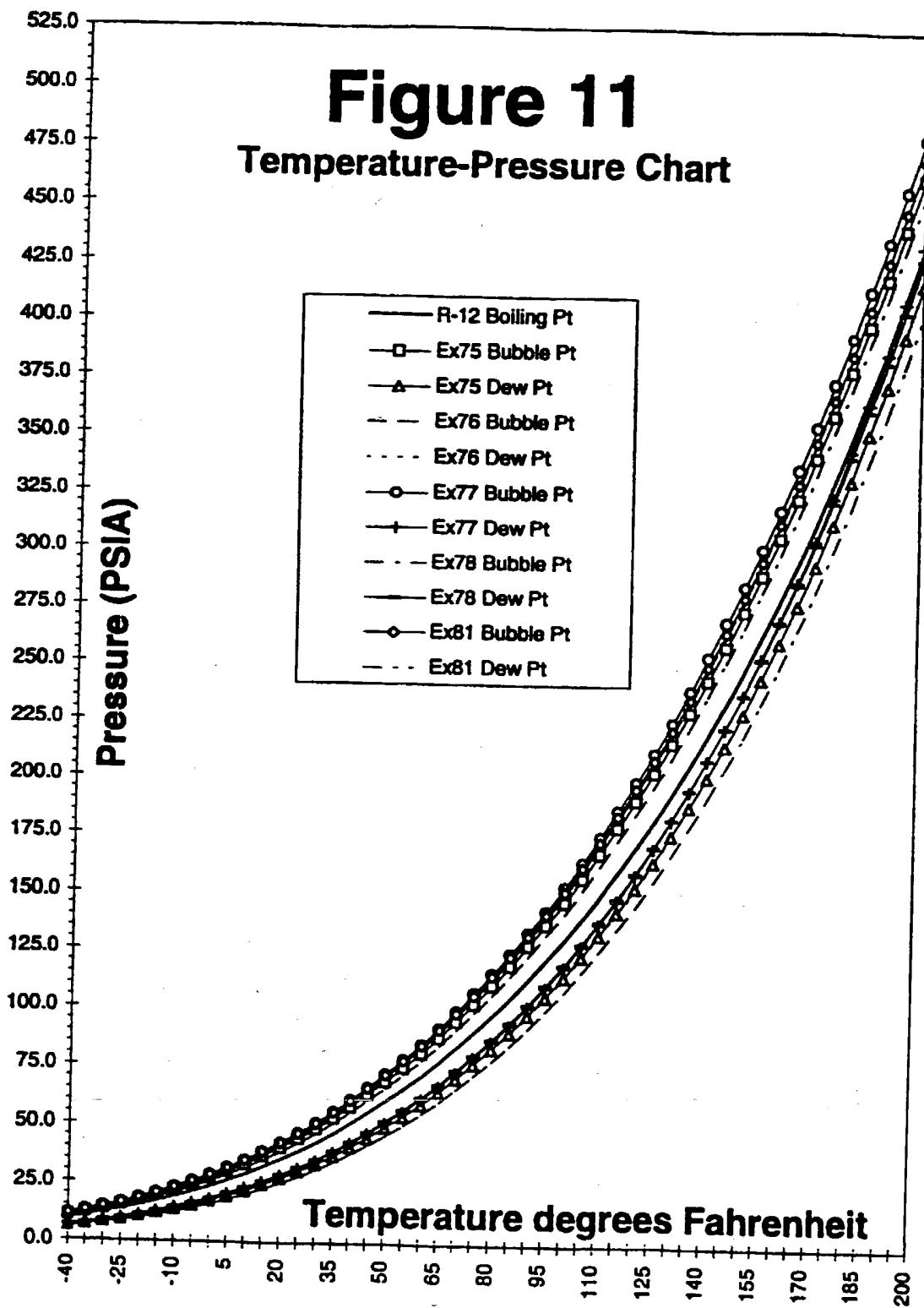


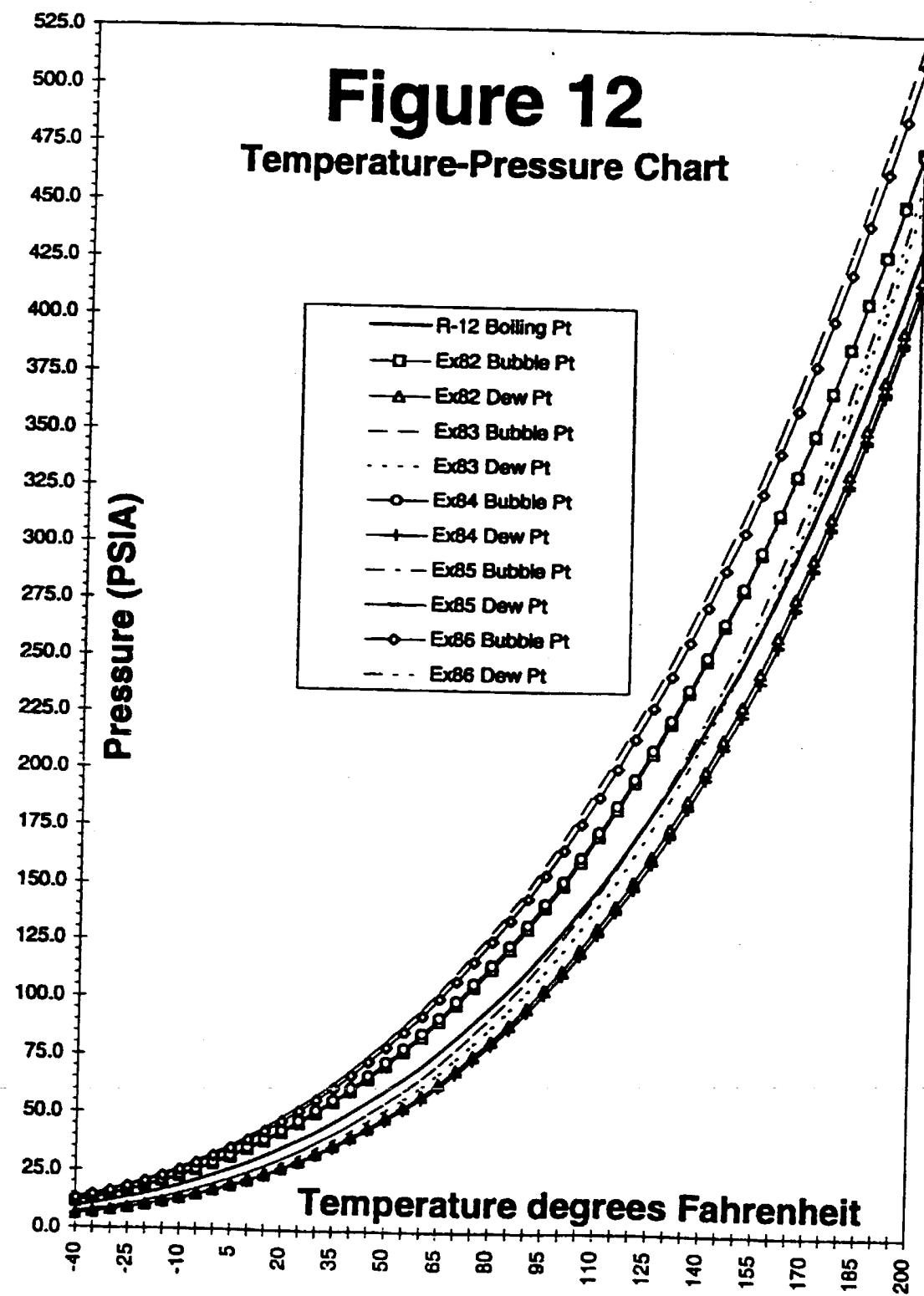


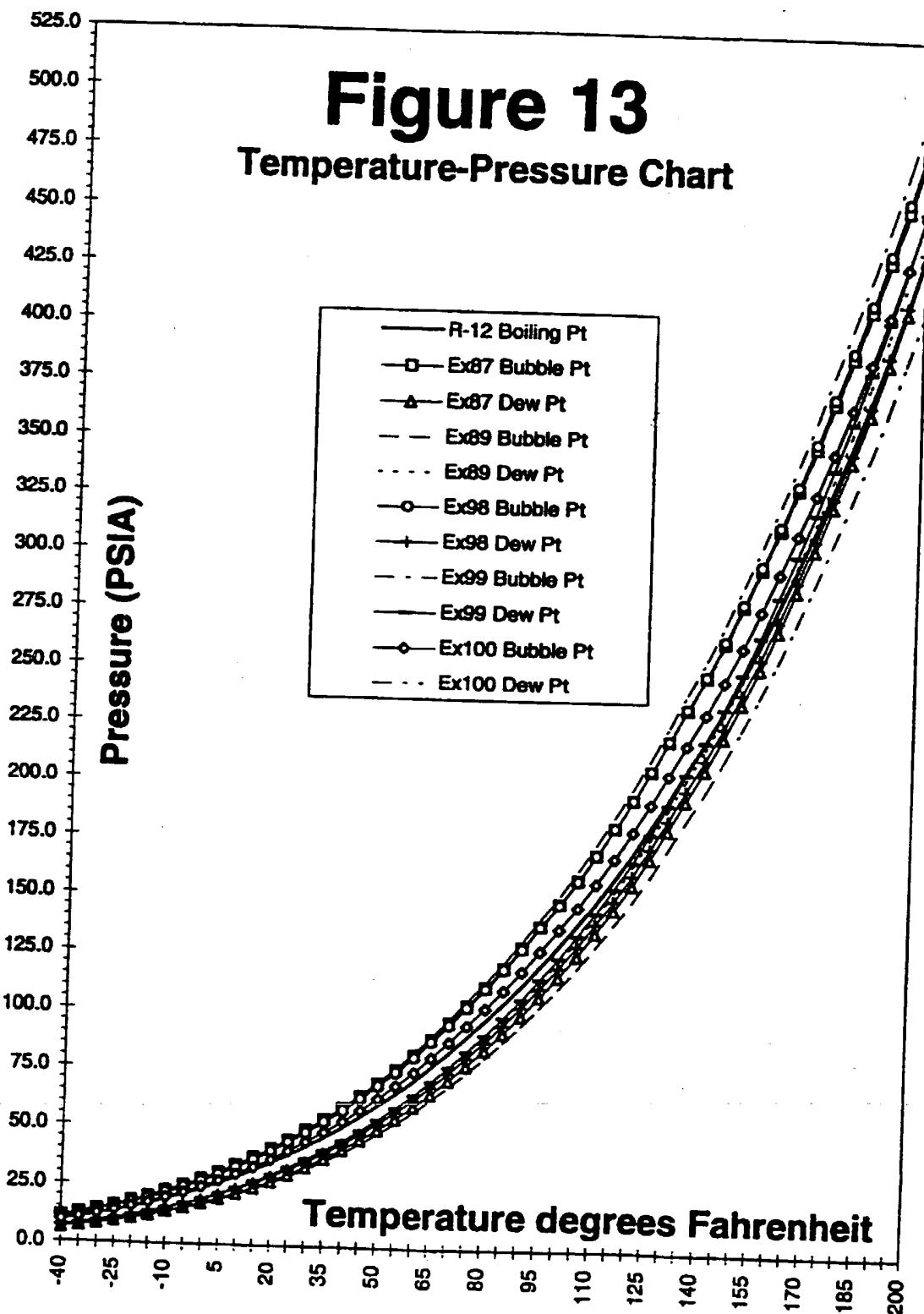


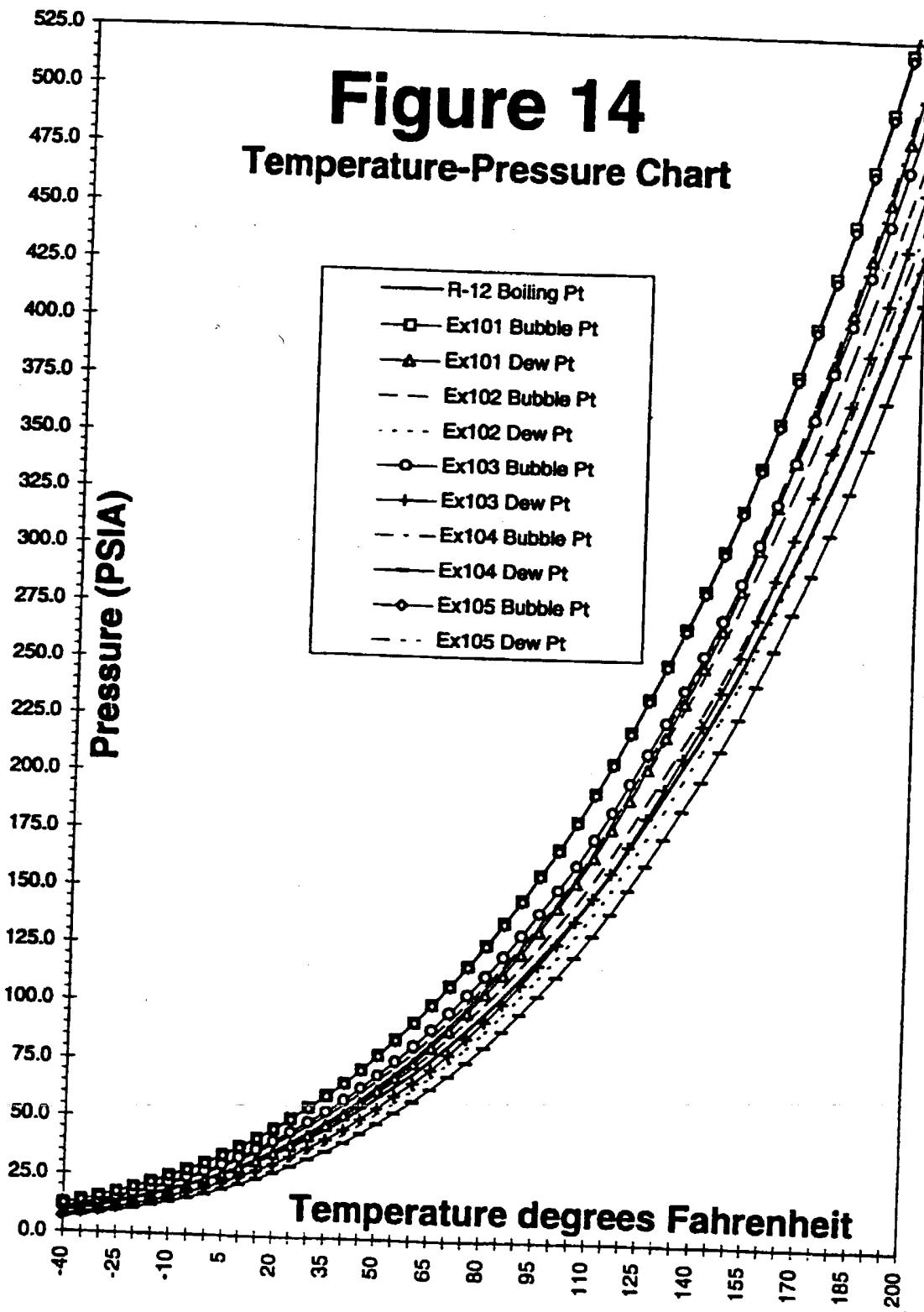


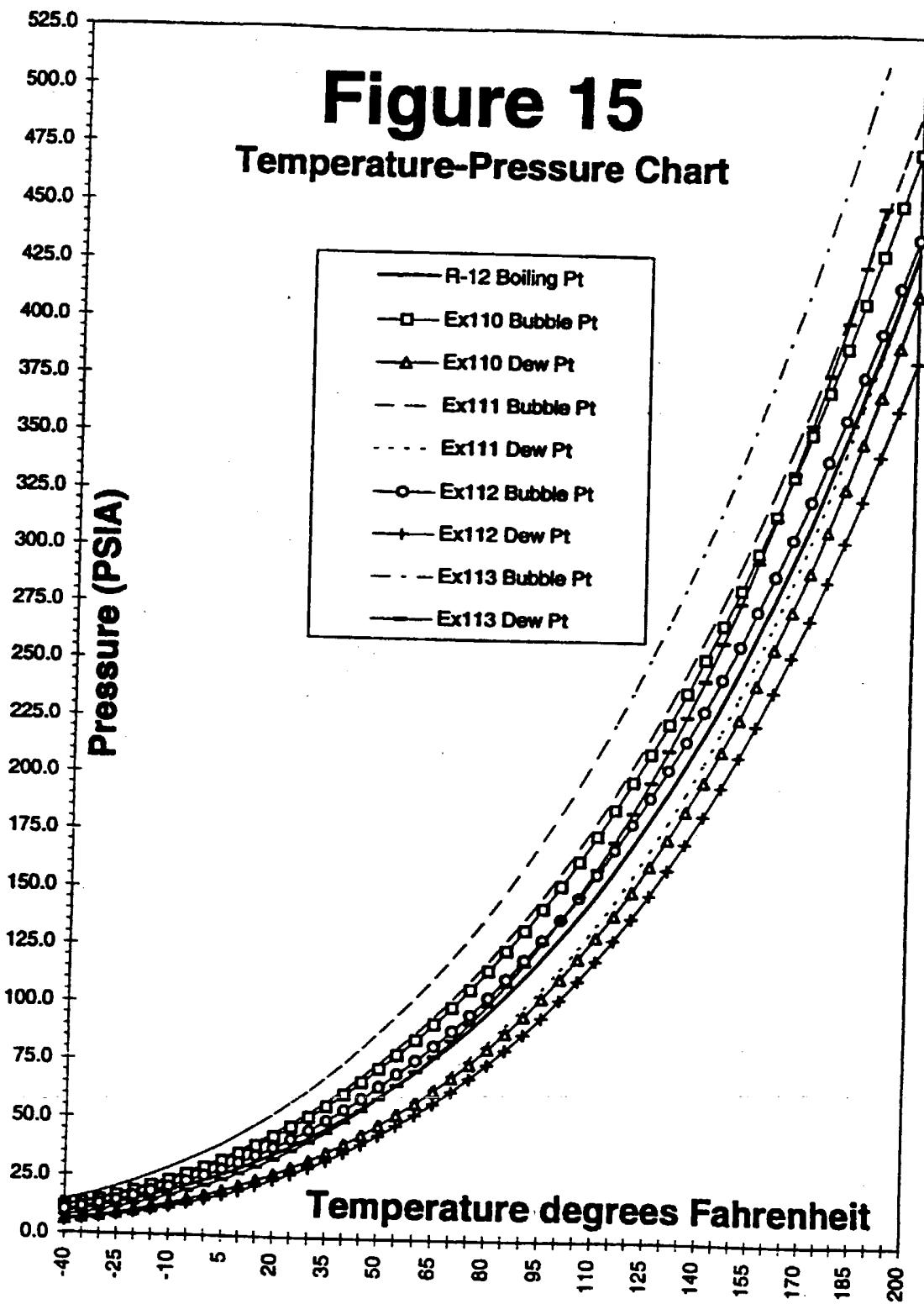












INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/14882

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C09K 5/04
US CL :252/67; 62/114

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/67; 62/114

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,214,929 A (GOBLE) 01 June 1993, Abstract.	1-10, 13, 61, 74
Y	US 5,151,207 A (GOBLE) 29 September 1992, Abstract.	1-10, 13, 61, 74
Y	US 4,303,536 A (ORFEO et al) 01 December 1981, col. 2, lines 31-41.	1-10, 13, 61, 74
Y	US 5,188,749 A (CROOKER) 23 February 1993, Abstract.	1-10, 13, 61, 74
Y	GB 2,228,739 A (PEARSON) September 1990, page 4 - page 5.	1-10, 13, 61, 74
Y	EP 0,619,356 A (BASILE et al) 12 October 1994, Abstract.	1-10, 13, 61, 74

 Further documents are listed in the continuation of Box C. See patent family annex.

Special categories of cited documents:	
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"Z"	document member of the same patent family

Date of the actual completion of the international search

30 JANUARY 1997

Date of mailing of the international search report

05 MAR 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer

Christine Skane

Telephone No. (703) 308-2526

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/14882

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0,105,831 A (ENJO et al) 18 April 1984, Abstract, page 1, Table 2.	1-10, 13, 61, 74
Y	US 4,482,465 A (GRAY) 13 November 1984, claim 6.	1-10, 13, 61, 74
Y	US 4,810,403 A (BIVENS et al) 07 March 1989, Table spanning column 3 to column 4.	1-10, 13, 61, 74
Y	WO 94/00529 A (ROBIN) 06 January 1994, page 3.	6-10, 61, 74
Y	US 5,277,834 (BIVENS et al) 11 January 1994, Abstract.	61
Y	US 5,061,394 A (BIVENS et al) 29 October 1991, Table 1.	9, 13
Y	BASILE et al, Chemical Abstracts, Vol. 122, No. 164680, "Quasi-azeotropic mixtures utilizable as refrigerating fluids", EP 638623, 15 February 1995, Abstract.	9, 13
A	US 5,417,871 (MINOR et al) 23 May 1995, Abstract.	1-10, 16, 74

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/14882

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
1-10, 13, 61, 74
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/14882

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

CAS ONLINE, DIALOG

search terms: isobutane, chlorodifluoroethane, chlorotetrafluoroethane, chlorodifluoromethane, heptafluoropropane, dimethyl ether